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Photolysis of iodomethane in the presence of oxygen in solid argon near 10 K has yielded several products detected by their vibrational absorption spectra. Isotopic labeling of reactants has proved methanal, water, hydrogen iodide, carbon monoxide, carbon dioxide, and hydroperoxyl radicals to be significant products, and a further set of major absorptions is attributed to hydrogen hypoiodite HOI, hydrogen-bonded to methanal. Other minor vibrational features are discussed, and a possible reaction scheme is briefly outlined.

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La photolyse de l'iodométhane, en présence d'oxygène dans l'argon solide près de 10 K, conduit à plusieurs produits détectés par leur spectre d'absorption vibrationnelle. Le marquage isotopique des réactifs a prouvé que le méthanal, l'eau, l'iodure d'hydrogène, le monoxyde de carbone, le dioxyde de carbone et des radicaux hypropéroxyles sont des produits importants; on a attribué un autre groupe majeur d'absorptions à de l'hypoiodite d'hydrogène (HOI) lié par pont hydrogène au méthanal. On discute d'autres vibrations mineures et on décrit un schéma réactionnel possible. [Traduit par le journal]

### Introduction

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In his investigation of photolysis of iodomethane in solid oxygen Roebber (1) postulated that several trapped radicals may have been produced, but lack of isotopically substituted reactants and problems of spectral range and resolution hampered positive identification. Also only a few trapped radicals were at that time characterized by vibrational spectra; even for many pertinent stable substances, reliable absorption spectra were available for neither gas phase nor argon matrix. Now that these conditions no longer prevail, we are able, in performing similar experiments, to identify several products unambiguously, and we have also obtained evidence for a previously undetected molecule which seems to be a major product.

#### Experimental

The apparatus consisted essentially of a refrigerator (Air Products Displex CS-202) mounted in an infrared spectrophotometer (Perkin-Elmer 225) and connected to both a metal high-vacuum pumping system and a glass manifold for sample preparation. In the conduct

of each experiment, after deposition of gases during 5-10 h, frozen samples were irradiated for 10-30 h (low pressure Hg lamp) and 1-2 h (HPK 125 lamp); the extent of photodecomposition of reactants and formation of products was measured by analysis of vibrational absorption spectra recorded before and after each irradiation operation. Flow of gases to the refrigerator was controlled by needle valves in the range 0.1-0.7 µmol s<sup>-1</sup>, monitored by Penning and Pirani pressure gauges. The gases were frozen on a Csl window in the refrigerator, held at 8-10 K (measured by a Chromel vs. 0.07% Fe/Au thermocouple). The irradiation sources were mercury arcs: Philips HPK 125, 125 W operating at a pressure  $\sim\!8\,\times\,10^{5}$  N m  $^{-2},$  or a specially constructed lamp, 8 W operating at a pressure of  $1.3 \times 10^3$  N m<sup>-2</sup> so as to emit principally at 39 412 and 54 069 cm<sup>-1</sup>. A filter transmitting 8 000-14 000 and 24 000-47 000 cm<sup>-1</sup> was occasionally used with the HPK 125 lamp. Spectral slit widths of the spectrometer varied from 0.3-1.5 cm<sup>-1</sup> in the range 200–4000 cm<sup>-1</sup>; wavenumber accuracy and reproducibility were 0.5 cm<sup>-1</sup> for sharp lines. Iodomethane  $(H_3^{12}CI \text{ from Fisher, } D_3^{12}CI \text{ from }$ 

Iodomethane  $(H_3^{12}CI \text{ from Fisher}, D_3^{12}CI \text{ from Merck}, Sharp and Dohme, and <math>H_3^{13}CI (86.3\% \text{ enrichment})$  from Prochem) was distilled and degassed before use.  ${}^{16}O_2$  was generated from  $KMnO_4$ ;  ${}^{18}O_2 (94 \text{ atomic}\% \text{ enrichment})$  was obtained from Yeda. Mixtures of  ${}^{16}O_2$ ,  ${}^{18}O_2$ , and  ${}^{16}O^{18}O$  (~40 atomic%  ${}^{18}O$  randomly distributed, as deduced from ozone byproduct composition) were prepared by electric discharge of  ${}^{16}O_2$  and  ${}^{18}O_2$ . Argon (Matheson, 99.998% nominal purity) was used directly from the cylinder.  $D_2^{12}CO$  was generated from polyoxymethylene- $d_2$  (Merck, Sharp and Dohme). Mixtures of iodomethane vapor (or  $D_2^{12}CO$ ) and argon, or oxygen and argon, were prepared and stored several hours before use.

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FIG. 2. Selected portions of the spectrum of  $D_3^{12}CI$ :  ${}^{16}O_2$ : Ar = 1:20:100. Upper spectrum, before photolysis; lower spectrum, sample had been irradiated for 30 h with the low-pressure Hg lamp and 2 h with the HPK 125 lamp.

### Results

Representative spectra recorded before and after irradiation of iodomethane-oxygen-argon mixtures are shown in Fig. 1 and 2. That a reaction had occurred after irradiation was clearly evident from the reduction in intensity of iodomethane lines and appearance of many new absorptions. (In contrast, when only iodomethane-argon mixtures were irradiated, no spectral changes were detected.) Characteristic growth patterns with the two radiation sources were observed for the new absorptions. By comparison of relative intensities during various photolytic operations within particular and between different experiments, lines exhibiting similar intensity patterns were grouped and are now presented in text and tables. Isotopic labeling of reactants permitted identification of produced substances; mixtures of both <sup>12</sup>Cand <sup>13</sup>C-containing iodomethane or all of <sup>16</sup>O<sub>2</sub>, <sup>18</sup>O<sub>2</sub>, and <sup>16</sup>O<sup>18</sup>O were particularly useful in indicating the number of either carbon or oxygen atoms in carriers of major absorption features. By this method, it was ascertained

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TABLE 1.	Absorption lines $(cm^{-1})$ of water molecules produced after
	irradiation of specified reactants*

H <sub>3</sub> <sup>12</sup> CI <sup>16</sup> O <sub>2</sub>	H <sub>3</sub> <sup>12</sup> CI <sup>18</sup> O <sub>2</sub>	H <sub>3</sub> <sup>13</sup> CI <sup>16</sup> O <sub>2</sub>	$D_3^{12}CI$	D <sub>3</sub> <sup>12</sup> CI <sup>18</sup> O <sub>2</sub>
3723.5 3712.7	3710 3700.4	3723.5 3714	2756	2742.5 2733
3700 br 3678 br	3687 br	3696 br 3678 br 2622	2718 br	2708 br
3614	3605	3614.3	2666 2640	2651
1615 br 1594.5	1615 br	1612 br 1595	1183 br	1177 br
1591 1585	1578.6	1591 1585	1176	_

\*In this and following tables, br = broad and sh = shoulder.

TABLE 2. Absorption lines (cm<sup>-1</sup>) of methanal molecules produced after irradiation of specified reactants, with reference lines

H <sub>3</sub> <sup>12</sup> CI <sup>16</sup> O <sub>2</sub>	$H_2^{12}CO$ (ref. 5)	H <sub>3</sub> <sup>12</sup> CI <sup>18</sup> O <sub>2</sub>	H <sub>3</sub> <sup>13</sup> CI <sup>16</sup> O <sub>2</sub>	D <sub>3</sub> <sup>12</sup> CI <sup>16</sup> O <sub>2</sub>	D <sub>2</sub> <sup>12</sup> CO (ref. 6)	D <sub>3</sub> <sup>12</sup> CI <sup>18</sup> O <sub>2</sub>
2882	2862	2865	2862.5	2200	2177	2200
2816.5	2796	2816.5	2812	2084	2069.7	2082.5
1735 sh	1742	1701	1697	1690	1697.8	
1728	1738	1695.5	1691	1682	1691.6	1645
1722.5 sh	1732	1690	1685.5	1677	1687.6	1640
1496	1498	1486	1496.4	1097.5	1099.4	1092.5
1492.5		1481.5	1492			
				990	987.1	982.5
1175.3	1167.5	1173.5	1163.5			

that no carrier of other than weak absorptions contained two or more carbon or oxygen atoms. Varying mole fractions of iodomethane and oxygen by dilution with argon was also helpful, a technique which Roebber (1) did not exploit.

Water, characterized by absorptions listed in Table 1, had both sharp lines at wavenumbers attributed to isolated molecules (2–4), and broad lines attributed to water hydrogen-bonded to other polar molecules within the same cavity bounded by argon and oxygen molecules. During an annealing operation, in which the sample temperature was allowed to rise to 20–30 K before recooling, sharp lines at 3712.7 and 3723.5 cm<sup>-1</sup> decreased in intensity, lines at 3678 and 3614 cm<sup>-1</sup> increased, and that at 3700 cm<sup>-1</sup> was little affected.

Methanal is also readily identified by its characteristic fundamentals, for which wavenumbers are listed in Table 2 and compared with published values (5, 6). Intensity measurements indicated dissimilar rates of iodomethane decomposition and methanal formation during irradiation. Simultaneous destruction of methanal by radiation from the HPK 125 lamp was confirmed in separate experiments with  $D_2CO:O_2:Ar$  samples.

Carbon monoxide and dioxide were both easily detected; wavenumbers are listed in Table 3. Atmospheric carbon dioxide hampered quantitative absorbance measurements in the 2350 and 667 cm<sup>-1</sup> regions, but there is no doubt that rates of carbon dioxide formation and of iodomethane decomposition were dissimilar. In fact, use of the HPK 125 lamp after the low-pressure lamp resulted in a relatively rapid increase of CO<sub>2</sub>. This behavior is consistent with its production via a secondary process.

Carbon monoxide lines are generally as previously reported (7-10), with slight variation attributed to matrix environment effects. An

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FIG. 3. Absorptions between 2050-2200 cm<sup>-1</sup> produced by photolysis of: (a)  $H_3^{12}CI^{16}O_2$ : Ar = 1:25:100; (b)  $H_3^{12}CI^{18}O_2$ : Ar = 1:13:110; (c)  $H_3^{13}CI^{16}O_2$ : Ar = 1:25:200.

TABLE 3. Absorption lines (cm<sup>-1</sup>) of carbon oxide molecules produced after irradiation of specified reactants

	H <sub>3</sub> <sup>12</sup> CI	H <sub>3</sub> <sup>12</sup> CI	H <sub>3</sub> <sup>13</sup> CI	D <sub>3</sub> <sup>12</sup> CI	D <sub>3</sub> <sup>12</sup> CI
	<sup>16</sup> O <sub>2</sub>	<sup>18</sup> O <sub>2</sub>	<sup>16</sup> O <sub>2</sub>	<sup>16</sup> O <sub>2</sub>	<sup>18</sup> O <sub>2</sub>
CO <sub>2</sub>	2341 662 652.5	2308* 645*	2776.5 643 635	2341 662.3	2308† 645*
C0	2152	2100.2	2105	2152.5	2100
	2147.5	2096.9	2100	2149†	2097.5
	2137.5	2086.5	2090	2137.5	‡

<sup>6</sup>Overlapped with  $C^{18}O_2$  initially present in  $^{18}O_2$  sample. †Obscured by D<sub>3</sub>Cl line. ‡Obscured by D<sub>2</sub>C<sup>18</sup>O absorption.

TABLE 4. Absorption lines (cm<sup>-1</sup>) of hydroperoxyl radicals produced after irradiation of specified reactants

$H_{3^{12}CI}$	H <sub>3</sub> <sup>12</sup> CI <sup>18</sup> O <sub>2</sub>	H <sub>3</sub> <sup>13</sup> CI <sup>16</sup> O <sub>2</sub>	D <sub>3</sub> <sup>12</sup> CI <sup>16</sup> O <sub>2</sub>
1390	1381	1390.0	
1388	1379.2	1388.3	
1100	1039.5	1100.5	1022

intense line at 2149 cm<sup>-1</sup> has been previously assigned to  ${}^{12}C^{16}O$  adjacent to  $H_2{}^{16}O$  (10), although a shoulder at 2152 cm<sup>-1</sup> has not previously been cited.

Underneath the fairly sharp lines assigned to  ${}^{12}C^{16}O$  was a broad line about 2138 cm<sup>-1</sup> with an apparent shoulder at 2125 cm<sup>-1</sup>. As shown in Fig. 3,  ${}^{18}O$ - or  ${}^{13}C$ - labeled reactants produced a shift of the CO lines leaving the broad line distinct. On the other hand, when  $D_3{}^{12}CI$  was used, this broad line disappeared,

but another appeared about 1525 cm<sup>-1</sup>, also unaffected by <sup>18</sup>O-labeled reactant. These observations lead to assignment of the absorbing species as hydrogen iodide (11). The breadth of the lines and shift from the gas-phase band center both indicate extensive hydrogen bonding.

Weak absorptions at wavenumbers noted in Table 4 indicate by their behavior on isotopic labeling that the carrier is the hydroperoxyl radical, consistent with similar wavenumbers measured in different experiments on this apparatus (12). Although lines were also found near the wavenumbers appropriate to OH and OD valence-stretching fundamentals of these radicals, that the peak intensities were anomalously large and that these lines were present when the lines listed in Table 4 were, in some experiments, absent strongly indicate that they belong to a different molecular carrier (*vide infra*).

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 TABLE 5. Absorption lines (cm<sup>-1</sup>) of methanoic acid produced after irradiation of specified reactants, with reference lines

$H_3^{12}CI_{16}O_2$	H <sup>12</sup> COOH* (ref. 13)	H <sub>3</sub> <sup>12</sup> CI <sup>18</sup> O <sub>2</sub>	H <sub>3</sub> <sup>13</sup> CI <sup>16</sup> O <sub>2</sub>	H <sup>13</sup> COOH* (ref. 13)	D <sub>3</sub> <sup>12</sup> CI <sup>16</sup> O <sub>2</sub>	D <sub>3</sub> <sup>12</sup> CI <sup>18</sup> O <sub>2</sub>
1748	1758	1715.5	1708.5	1715	1710	1679.5
1121 1118.5	1129	1089.5 1086	1111.8 1108.8	1117		

\*In carbon monoxide matrix.

TABLE 6. Absorption lines (cm<sup>-1</sup>) tentatively attributed to hydrogen hypoiodite molecules produced after irradiation of specified reactants

$H_{3}^{12}CI$ $^{16}O_{2}$	H <sub>3</sub> <sup>12</sup> CI <sup>18</sup> O <sub>2</sub>	H <sub>3</sub> <sup>13</sup> CI <sup>16</sup> O <sub>2</sub>	D <sub>3</sub> <sup>12</sup> CI <sup>16</sup> O <sub>2</sub>	D <sub>3</sub> <sup>12</sup> CI <sup>18</sup> O <sub>2</sub>
3417	3406	3417	2524.5	2513.5 sh 2508
1193	1191	1193	874.5	868
571.3	543.1	571.3	566.5	539.8

Some weak lines listed in Table 5 appear to be due to the s-transoid rotamer of methanoic acid (HCOOH and DCOOD), by comparison with results obtained for a carbon monoxide matrix (13) and the vapor phase (14).

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matrix (13) and the vapor phase (14). A weak line at 1304 cm<sup>-1</sup> in H<sub>3</sub><sup>12</sup>CI experiments which was insensitive to <sup>18</sup>O presence but which shifted to 1296 cm<sup>-1</sup> when H<sub>3</sub><sup>13</sup>CI was used is attributed to methane (15). The lines were relatively most intense when the mole fraction of oxygen in the argon matrix was smallest. Other fundamentals of CH<sub>4</sub> or CD<sub>4</sub> would have been masked by absorptions of H<sub>3</sub>CI, D<sub>3</sub>CI, or D<sub>2</sub>CO present in greater abundance.

Weak lines at 1032 and 1038 cm<sup>-1</sup>, unaffected by <sup>13</sup>C- or D-labeled reactants were observed after irradiation with the low-pressure Hg lamp when oxygen mole fractions were relatively large, and even when iodomethane was absent. Assignment to ozone is consistent with known argon matrix wavenumbers (16).

The remaining lines detected after irradiation are not easily assigned to specific known molecules. One group of these, listed in Table 6, was fairly intense and had similar intensity behavior during various operations and under varied experimental conditions. Selected regions of spectra illustrated in Figs. 1 and 2 show these lines obtained from two sets of isotopically labeled reactants.

Other lines, listed in Table 7, are difficult

to assign to particular molecules, but the wavenumber values and isotope shift do provide some clues to the nature of the chromophores.

## Discussion

## Tentative Identification of Hydrogen Hypoiodite

The lines in Table 6 may be analyzed according to the wavenumber positions and isotope effects as follows. The lines near 3400 and  $2500 \text{ cm}^{-1}$  are obviously O—H and O—D stretching modes. The lines between 540 and 575 cm<sup>-1</sup> are suitable for O–I valence-stretching modes; these values are similar both to the mean, 504 cm<sup>-1</sup>, of wavenumbers of symmetric and antisymmetric stretching modes of IO<sub>2</sub>containing molecules (17), and to the single fundamental of the IO free radical, 673 and  $504 \text{ cm}^{-1}$ , in its two characterized electronic states (18). The lines near 1190 and  $870 \text{ cm}^{-1}$ are appropriate to a deformation mode in which most of the amplitude (and kinetic energy) of vibration belongs to the H and D atoms. All lines are insensitive to <sup>13</sup>C-labeling, indicative of absence of carbon in the carrier. When <sup>16</sup>O- and <sup>18</sup>O-reactants, including <sup>16</sup>O<sub>2</sub>, <sup>18</sup>O<sub>2</sub>, and <sup>16</sup>O<sup>18</sup>O, were used, no further lines were produced; thus the carrier contains a single oxygen atom. The best estimate of the carrier consistent with these observations is hydrogen hypoiodite HOI. Two further broad lines, near  $502 \text{ cm}^{-1}$ in  $H_3CI$  and 377 cm<sup>-1</sup> in  $D_3CI$  experiments, seem to have similar intensity behavior to the

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H <sub>3</sub> <sup>12</sup> CI <sup>16</sup> O <sub>2</sub>	H <sub>3</sub> <sup>12</sup> CI <sup>18</sup> O <sub>2</sub>	H <sub>3</sub> <sup>13</sup> CI <sup>16</sup> O <sub>2</sub>	D <sub>3</sub> <sup>12</sup> CI <sup>16</sup> O <sub>2</sub>	D <sub>3</sub> <sup>12</sup> CI <sup>18</sup> O <sub>2</sub>
3544	3532	3544		
3351 br	3338 br	3351 br	2475 br	2462 br
1754	1721	1714		
1050	1049	1050	770	
839.3	795.1	838.4	837	795.7
			835	
801.5	760	801.5	799.8	759.3
587	557	587	573	546
562.3	536.5	563	556	530
553.5		553.8	548	522.3

TABLE 7.	Absorption lines (cm <sup>-1</sup> ) of miscellaneous species produced
	after irradiation of specified reactants

lines in Table 6, but show no <sup>18</sup>O shift, perhaps because of their breadth. The large deuterium isotope shift is appropriate to a H- or Dstretching or, more likely in this wavenumber region, deformation mode. The breadth of these two lines suggests strongly hydrogenbonded interactions. Because of the line breadth and insensitivity to <sup>18</sup>O-labeling, these lines will be assumed not to belong to the same carrier, in the same environment, as the lines in Table 6.

On the basis of assignment of these twelve lines to four isotopic varieties of hydrogen hypoiodite with a common vibrational force field, a complete normal coordinate analysis has been conducted. The results (19) include a fit of these wavenumbers to 0.2% accuracy and a potential energy distribution entirely consistent with the above deductions. Comparison of the force field parameters obtained thus for HOI with those for the other hydrogen hypohalites HOF, HOCI, and HOBr, all with  $\sim 0.2\%$  fitting accuracy, shows gradual periodic trends expected for such a family of simple molecules. These results are taken as strong support for the identification of the new carrier as stated.

## Other Unidentified Products

Sharp but weak lines between 760 and  $840 \text{ cm}^{-1}$  (cf. Table 7) appeared during irradiation with the low-pressure Hg lamp but disappeared rapidly when the HPK 125 lamp was used. Isotopic shifts are appropriate to either O—O or I==O vibrations. We expect the O—O bond to be much more susceptible to rupture by near ultraviolet radiation, copiously emitted by the HPK 125 lamp, than the I==O bond. H<sub>3</sub><sup>12</sup>COOH and D<sub>3</sub><sup>12</sup>COOD absorb

at 820 and  $794 \text{ cm}^{-1}$  respectively (20); the measured deuterium shifts are much smaller. Other peroxides expected to absorb in this region are the radical H<sub>3</sub>COO and its iodide H<sub>3</sub>COOI.

Lines near 3350 or 2475 cm<sup>-1</sup> were relatively broad, presumably indicative of OH or OD groups involved in hydrogen bonding. Two weak lines at 1754 and 1054 cm<sup>-1</sup> (and their isotopic counterparts) gave measurable absorbances in experiments only with larger oxygen mole fractions (~0.25) but they do not necessarily belong to the same carrier. The former line exhibited shifts appropriate to a carbonyl stretching mode, whereas the broader line at 1050 cm<sup>-1</sup> seemed to be unaffected by <sup>13</sup>C-labeling.

Groups of lines between 500 and  $600 \text{ cm}^{-1}$  are much more sensitive to <sup>18</sup>O-presence than to <sup>13</sup>C-labeling, indicative of O—I vibrations for instance, but not C—I. Their carriers may be further iodine oxides or oxyacids, but absorbance effects on annealing do indicate that a few different species are involved.

# Mechanism of Photolytic and Oxidation Processes

A full treatment of the reactions must explain the production of the following species definitely detected:  $H_2O$ ,  $H_2CO$ , CO,  $CO_2$ , HI,  $HO_2$ ,  $O_3$ ; and the probable detection of HOI, HCOOH,  $CH_4$ , some peroxide; but the absence of  $CH_3$ , OI, HCO, OH,  $H_2O_2$ ,  $H_2O_3$ ,  $H_2O_4$ ,  $HIO_2$ ,  $HIO_3$ ,  $HIO_4$ . The following set of reactions briefly summarizes a reasonable, but not unique, explanation of the product distribution under the conditions of these experiments:

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hν [1]  $H_3CI + O_2 \rightarrow [CH_3 + O_2 + I]$  $\rightarrow \begin{cases} H_3COO + I \\ \text{or } H_3COOI \end{cases} \stackrel{hv}{\rightarrow} ] H_2CO + HOI \end{cases}$  $H_2CO \rightarrow H_2 + CO$ [2]  $H_2CO + O_2 \rightarrow H_2O + CO_2$ [3]  $H_3CI + O_2 \rightarrow [CH_2 + O_2 + HI \rightarrow] HCOOH + HI$ [4]  $HCOOH \rightarrow H_2O + CO$ [5] hν  $HI \rightarrow H + I$ [6]  $H + H_3CI \rightarrow CH_4 + I$  $H + O_2 \rightarrow HO_2$ hν  $O_2 \rightarrow O + O$ [7]  $O + O_2 \rightarrow O_3$ hν  $HOI \rightarrow OH + I$ [8]  $\mathrm{OH} + \mathrm{I} + \mathrm{H_2CO} \rightarrow \mathrm{H_2O} + \mathrm{CO} + \mathrm{HI}$  $\rightarrow$  HCOOH + HI hν

[9]  $H_3CI \rightarrow H_3C + I \rightarrow H_3CI$  (recombination)

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Separate experiments with one of  $H_3CI$ ,  $O_2$ , or  $D_2CO$  in argon justify inclusion of reactions 2, 7, and 9, and experiments on  $D_2CO$  and  $O_2$  in Ar for [3]. This reaction scheme may be compared with those proposed for the gas phase photo-oxidation of iodomethane (21–23). Whether ozone was produced only directly from oxygen in experiments with iodomethane could not be ascertained.

Evidence exists for the production of both  $H_2CO$  and HOI in the same matrix cage in that widths of HOI lines were greater than those of, for instance, ozone, and the shifts of some methanal vibrations from wavenumbers associated with isolated molecules in solid argon (5, 6). These effects suggest a hydrogen-bonded interaction of form

The resulting perturbation of HOI wavenumbers probably does not appreciably affect the force field parameters calculated from these measurements (19).

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