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Photochemical Isomerization of Dihalomethanes in Argon Matrices

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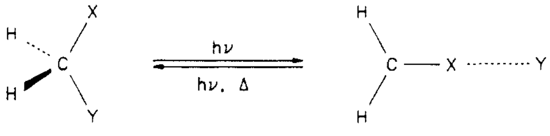
Abstract: It was found that photolysis of various dihalomethanes in an argon matrix at 12 K gives rise to isomeric species. Ab initio calculations indicate that in these isomers one halogen has been removed from the carbon and forms a weak bond with the other halogen on the carbon. This is supported by comparison of the observed IR spectra of the photoisomers with those calculated by ab initio methods.

I. Introduction

Diiodomethane is well-known as a reagent for cyclopropanation in the classical Simmons–Smith reaction.[1] In 1965 Simmons found that photolysis of diiodomethane in the presence of olefins also yields cyclopropanes with high stereospecificity,[2] and he postulated either a free methylene or an excited diiodomethane as an intermediate. Pienta and Kropp, who improved the method in 1978, proposed an iodocarbenium–iodide ion pair as an intermediate.[3] On the other hand in many papers dealing with the photolysis of diiodomethane in the gas phase, it has been shown that the primary step is the homolytic cleavage of the C–I bond, giving rise to the iodomethyl radical and an iodine atom.[4] Hence, the mechanism of the photolysis might be different in the gas phase from that in the condensed phase. This diversity is additionally supported by the observation that on irradiation of diiodomethane and other halomethanes in matrices at 15 or 77 K intense colors are developed that disappear on heating.[5] The origin of the colored species was explained by the formation of molecular cations and radicals.[5] But since the energy of the light used in the experiments was far less than of the ionization potential of the halomethane precursors, a rather unlikely many step mechanism had to be constructed.

As we have shown recently,[6] it is possible to photoisomerize the iodohalomethanes **1a–c**[6a] or tetrachloromethane[6b] in an argon or nitrogen matrix. The photoisomers can be described as the isohalomethanes **2a–c**. In this paper we give a full account of the UV/vis and IR spectroscopic study of the photolysis of the halomethanes **1a–g** isolated in rare-gas matrices. In all cases (except **1d**) the same type of photoreaction occurs, and it appears that the newly formed colored species are always distinct isomers. In order to support the experimental results, the IR spectra of the photoisomers of dibromomethane (**2e**), bromochloromethane (**2f**), dichloromethane (**2g**), and tetrachloromethane[6b] have been studied by ab initio methods. It turns out that there is indeed an alternative to the tetrahedral arrangement of the four substituents in the halomethanes. In all four examples an energy minimum was found with a nonplanar C_s geometry.



1a–g *2a–g*

	a	b	c	d	e	f	g
X =	I	Br	Cl	F	Br	Cl	Cl
Y =	I	I	I	I	Br	Br	Cl

II. Calculations

All calculations were performed with the program CADPAC[7] on an SCS-40 computer. For **2e–g**, stationary points were located (SCF/6-31G* and MP2/6-31G*) with a C_s symmetry constraint. The plane of symmetry contained the carbon and two halogen atoms. All were confirmed to be minima on their respective potential surfaces by finding all computed vibrational frequencies to be real. Geometries and energies obtained are given in Table I.

These isodihalomethanes are high-energy species, and their estimated stabilities depend upon whether or not the energy needed for their formation would instead fragment the parent diholomethane into a halomethyl radical and a halogen atom. Table II compares the energy differences between the isodihalomethanes and the dihalomethanes to the bond dissociation energies of the dihalomethanes. The comparison is not as precise as one would like since the theoretical energies refer to differences between fixed-nuclear calculations with no vibrational, rotational, or translational corrections. Further, the experimental bond energies were not all obtained in the same way and do not all measure quite the same thing. Nevertheless, the isodihalomethanes do all appear to have slightly less energy than needed to break a halogen bond in the parent dihalomethane and, hence, should show some stability.

III. Experimental Observations

Iodohalomethanes. The iodohalomethanes **1a–d** show absorption bands in the UV region between 295 and 255 nm due to an $n \rightarrow \sigma^*$ transition of the C–I bond. On irradiation of the matrix-isolated compounds **1a–c** with monochromatic light corresponding to the long-wavelength part of each absorption band, the matrices

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(1) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256.

(2) Blomstrom, D. E.; Herbig, K.; Simmons, H. E. *J. Org. Chem.* **1965**, *30*, 959.

(3) (a) Pienta, N. J.; Kropp, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 655. (b) Kropp, P. J.; Pienta, N. J.; Sawyer, J. A.; Polniaszek, R. P. *Tetrahedron* **1981**, *37*, 3229. (c) Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131.

(4) (a) Kroger, P. M.; Demou, P. C.; Riley, S. J. *J. Chem. Phys.* **1976**, *65*, 1823. (b) Schmitt, G.; Comes, F. J. *J. Mol. Struct.* **1980**, *61*, 51. (c) Schmitt, G.; Comes, F. J. *J. Photochem.* **1980**, *14*, 107. (d) Nolte, R.; Seibert, A.; Seidel, W. *Z. Naturforsch.* **1983**, *38a*, 591.

(5) (a) Brown, G. P.; Simons, J. P. *Trans. Faraday Soc.* **1969**, *65*, 3245. (b) Andrews, L.; Prochaska, F. T.; Ault, B. S. *J. Am. Chem. Soc.* **1979**, *101*, 9. (c) Mohan, H.; Rao, K. N.; Iyer, R. M. *Radiat. Phys. Chem.* **1984**, *23*, 505.

(6) (a) Maier, G.; Reisenauer, H. P. *Angew. Chem.* **1986**, *98*, 829; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 814. (b) Maier, G.; Reisenauer, H. P.; Hu, J.; Hess, B. A., Jr.; Schaad, L. J. *Tetrahedron Lett.* **1989**, *30*, 4105.

(7) Amos, R. D.; Rice, J. E. CADPAC, issue 4.0, University of Cambridge.

(8) Weissman, M.; Benson, S. W. *J. Phys. Chem.* **1983**, *87*, 243.

(9) Kaposi, O.; Riedel, M.; Sanchez, G. R. *Magy. Kem. Foly.* **1974**, *80*, 419; *Chem. Abstr.* **1975**, *82*, 42714.

(10) Szwarc, M.; Sehon, A. H. *J. Chem. Phys.* **1951**, *19*, 656.

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Table I. Computed Geometries of the Isodihalomethanes **2e–2g**[a]

	H_2CBr–Br (**2e**)		H_2CCl–Br (**2f**)		H_2CCl–Cl (**2g**)	
parameter	SCF/6-31G*	MP2/6-31G*	SCF/6-31G*	MP2/6-31G*	SCF/6-31G*	MP2/6-31G*
R_{C-H}	1.0715	1.0817	1.0726	1.0830	1.0721	1.0830
R_{C-X}	1.7340	1.7853	1.5713	1.6284	1.5794	1.6471
R_{X-Y}	2.8227	2.7816	2.5761	2.4150	2.7336	2.6309
∠HCX	118.98	117.44	119.46	117.68	119.28	117.02
∠HCH	120.30	121.71	120.41	121.63	120.64	121.49
α^b	13.26	18.89	8.22	17.72	8.92	21.62
∠CXY	122.42	118.30	121.76	119.94	122.87	121.37
total energy	−5183.54084	−5184.56248	−3070.69987	−3071.42569	−957.84067	−958.28479

[a] Bond distances in angstroms, angles in degrees, energies in atomic units. [b] The angle made by X and the bisector of the HCH plane.

Table II. Energy Comparisons of the Isodihalomethanes $CH_2X\cdots Y$ (kcal/mol)

	X = Y = Cl (**2g**)	X = Y = Br (**2e**)	X = Cl, Y = Br, (**2f**)
$E(CH_2X\cdots Y)-E(CH_2XY)^a$			
MP2/6-31G*(full core)// MP2/6-31G* (full core)[b]	72.7	61.2	65.6
MP4/6-31G*(frozen core)// MP2/6-31G* (full core)	68.2	54.8	57.9
experimental bond energy (CH_2X–Y)	82.8[c]	64 ± 4[d]	60.1[e]

[a] Energies of lowest point in potential wells. [b] This notation means that a calculation of the kind shown before the double slash was carried out at the optimum geometry of the calculation shown after the double slash. [c] Reference 8; ΔH_{298} for bond breaking. [d] Reference 9; presumably a ΔH value. [e] Reference 10; Arrhenius activation energy.

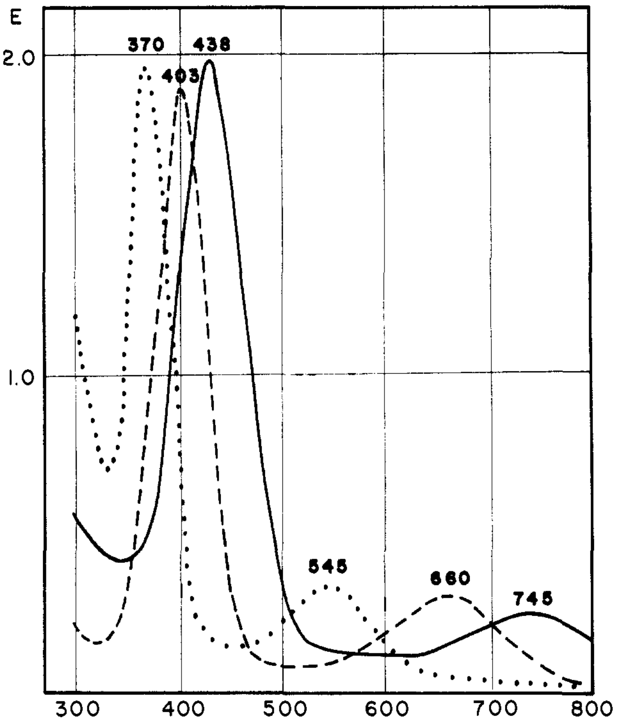


Figure 1. UV spectra (N_2 matrices, 12 K) of the isomers **2a** [(···), 0.5-min irradiation, violet matrix], **2b** [(- - -), 10-min irradiation, green matrix], and **2c** [(—), 25-min irradiation, yellow matrix].

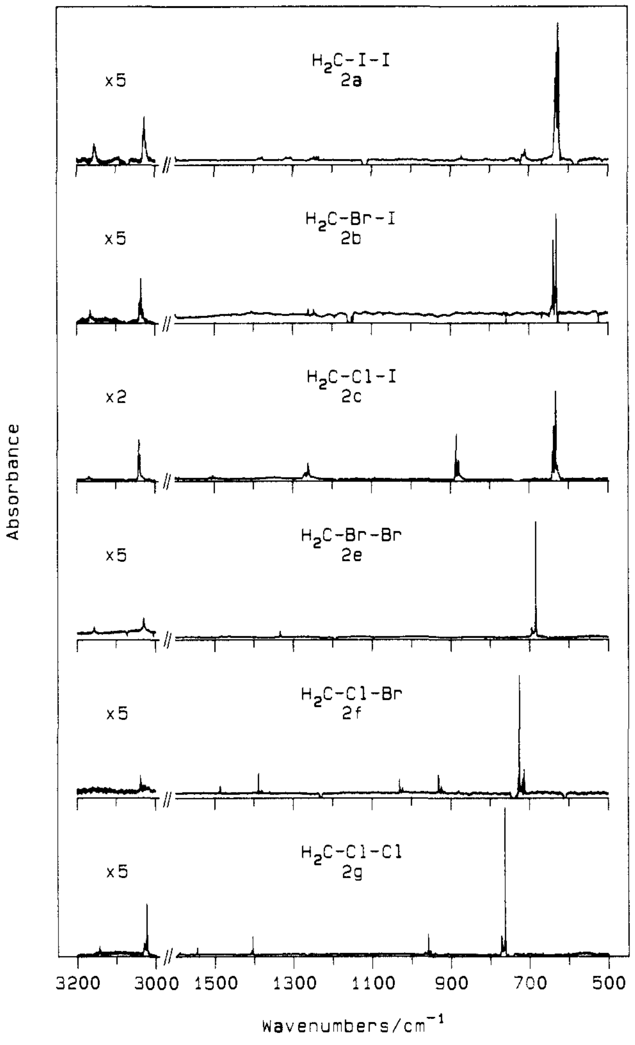


Figure 2. Experimental IR spectra of the isodihalomethanes **2a–2c** and **2e–2g** (difference spectra of the back-reaction **2** → **1**).

immediately become colored because of the electronic absorption of the new species **2a–c** (**2a**, violet; **2b**, green; **2c**, yellow; cf. Figure 1). On prolonged irradiation a photoequilibrium is obtained that is strongly dependent on the wavelength used. With an optimized wavelength, a conversion of about 30% can be achieved. Despite its seemingly favorable absorption maximum at 255 nm, fluoroiodomethane (**1d**) does not afford even a trace of the photoisomer **2d**.

The electronic excitation spectra of **2a–c** (Figure 1) are very similar with a weak long-wavelength band ($\epsilon \sim 1300$) and a strong band ($\epsilon \sim 10000$) at higher energy, both with bathochromic shifts going from **2a** to **2c**. Upon subsequent irradiation of the matrices with light corresponding to one of the absorptions bands of the photoisomers **2a–c** or with white light, they rapidly lose their colors and both UV/vis and IR spectroscopy reveal an almost quantitative re-formation of **1a–c**. This observation strongly suggests that compounds **1** and **2** must be isomers.

The IR bands of the photoisomers **2a–c** can be deduced by examining the difference spectra obtained from the irradiated and nonirradiated matrices (forward reaction) and from those of the backward reaction. In this way it is possible to rule out bands arising from secondary photoproducts of **2** or other minor byproducts. The spectra so obtained have the same appearances (Figures 2 and 3): two bands in the C–H stretching region (3028–3042 and 3168–3150 cm^{-1}), which show the expected shifts to 2213–2228 and 2377–2395 cm^{-1} upon deuteration, and a very strong absorption at 610–640 cm^{-1}, which also shows a large

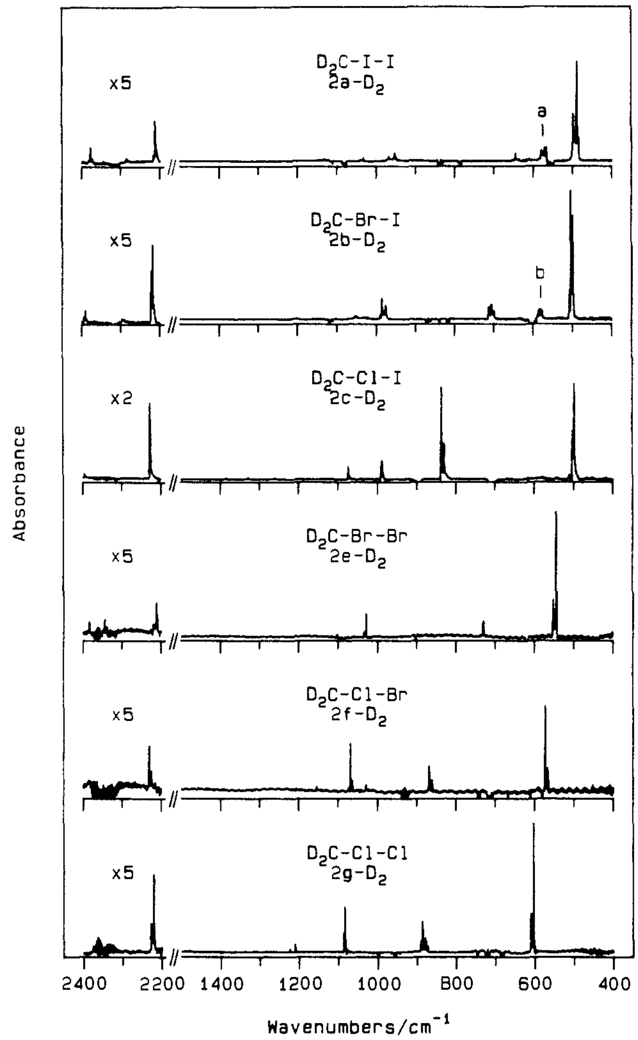


Figure 3. Experimental IR spectra of the deuterated isodihalomethanes **2a**-d_2–**2c**-d_2 and **2e**-d_2–**2g**-d_2 (difference spectra of the back-reaction **2** → **1**): (a) **2a**-d, (b) **2b**-d.

deuterium shift. The rather intense first overtone of this band can be observed in all spectra. The splittings of the IR bands are caused by matrix effects (different sites) as can be shown by annealing the matrices yielding irreversible changes of the relative intensities within each group of bands. In the spectrum of chloroiodo derivative **2c** an additional strong band around 880 cm^{-1} is present. It is shifted by only 50 cm^{-1} upon deuteration. The splitting of this absorption into two main bands (**2c**, 886.2/879.4 cm^{-1}; **2c**-d_2, 836.5 cm^{-1}) with the intensity ratio of 3:1 allows its assignment to a C–Cl stretching vibration (^{35}Cl/^{37}Cl isotopes in natural abundance). These bands are further distorted by matrix effects, but by careful monitoring of the intensity changes during the annealing process, it is possible to distinguish between matrix effects and isotopic splitting.

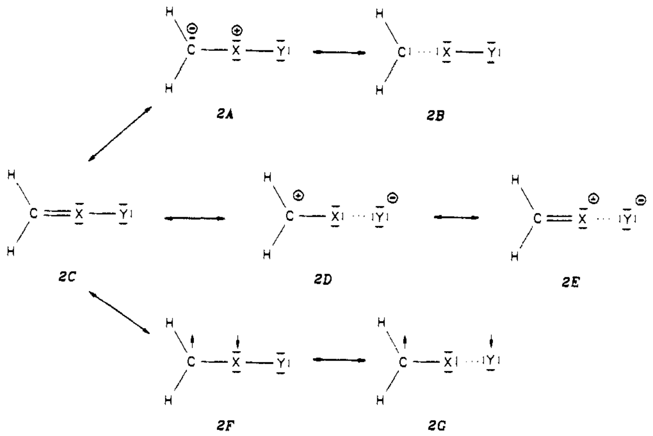
To obtain a rough idea of the thermal stability of the photoisomers, the photochemical interconversion **1a** → **2a** was carried out in a polyethylene matrix at 13 K, yielding the same results as in the argon matrix. When the sample was warmed, the UV/vis and IR absorption bands of **2a** began to vanish at temperatures above 100 K ($t_{1/2}$: at 100 K, 4 h; at 120 K, 1 h; at 140 K, 5 min). In the process at least a partial re-formation of **1a** occurred, as revealed by IR spectra. The thermal stability of **2b** and **2c** turned out to be much lower. The back-reaction **2c** → **1c** could be observed upon warming of the argon matrix to only 26–30 K.

Other Dihalomethanes. The electronic absorptions of dibromo- (**1e**, λ_{max} = 220 nm), bromochloro- (**1f**, λ_{max} = 203 nm), and dichloromethane (**1g**, λ_{max} < 200 nm) appear at shorter wavelengths than the iodine-containing compounds. Hence, the mercury and xenon lamps used for the photoexcitation are much less efficient for the photoconversion of these compounds. With 240- or 230-nm light, long irradiation times of hours are necessary to isomerize **1e** and **1f**. In the photoequilibrium, less than 10% is converted to **2e** and **2f**. The isomerization of dichloromethane (**1g**) to isodichloromethane (**2g**) can be achieved with the 185-nm line of a mercury lamp (interference filter) or with 193-nm light from an ArF excimer laser. After an irradiation time of 8 h (Hg lamp, conversion 10%) or 7 min (laser, conversion 6%) the photoequilibrium **1g** ⇄ **2g** is reached.

The UV/vis spectra show new absorption bands at 360 nm (**2e** and **2g**) and at 382 nm (**2f**). The expected weaker long-wavelength bands can only be detected in the spectrum of **2g** at about 620 nm. In the other two cases their presence can be deduced from the fact that the back-reaction of the isomers can be caused not only with 360-nm light but also with light of wavelength greater than 570 nm. The similarity of their infrared spectra with those of **2a–c** (Figures 2 and 3) also indicates that the analogous photoisomerization takes place. Again two CH stretching vibrations can be observed for the dibromo and the dichloro compounds. (For **2f** only the stronger one at 3038.6 cm^{-1} can be recorded because of the low signal to noise ratio in the spectrum.) The strongest bands appear around 700 cm^{-1}. These are of somewhat higher values than those of **2a–c** and are shifted by about 150 cm^{-1} upon deuteration. As in the spectrum of **2c**, CCl stretching bands with an isotopic splitting due to the ^{35}Cl/^{37}Cl isotopes and with smaller deuterium shifts of 50–70 cm^{-1} are also found for **2f** and **2g**.

IV. Nature of the Photoisomers

From the reversibility of the photoreaction **1** ⇄ **2** and the thermal back-reaction **2** → **1**, which can be observed in some cases, it is probable that the new species **2** and the precursors **1** are isomers. Seven possible resonance structures for **2** may be



considered: **2A** symbolizes a halonium ylide, **2B** indicates a weak complex between a carbene and a halogen, **2C** describes a hypervalent species, **2D** and **2E** can be formulated as contact ion pairs, **2F** has the double bond of **2E** decoupled, and **2G** is a resonance structure that can be taken as a radical pair. Whereas in **2A** and **2B** the carbon atom bears a negative charge, the reverse polarization must be found if contact ion pairs **2D** or **2E** are more important. Indeed, these two as shown below contribute primarily to the actual structure.

Dihalomethanes. Information about the nature of the photoisomers is provided by their IR spectra. Since their appearance is roughly the same for all the isodihalomethanes, band assignments will be made with the calculated IR spectra of the dibromo, bromochloro, and dichloro derivatives **2e–g**. Taking into account that the calculated IR frequencies are normally about 10% too high, the overall fitting of the pattern of the calculated and experimental spectra (Figures 4–9) is good and leaves little doubt about the proposed structures. This is especially true for the MP2/6-31G* spectra of **2f** and **2g**. Unfortunately, an attempt to calculate the MP2/6-31G* spectrum of **2e** failed because of insufficient disk space.

The calculations predict that both CH stretching vibrations should be well separated by about 150 cm^{-1} and that the more

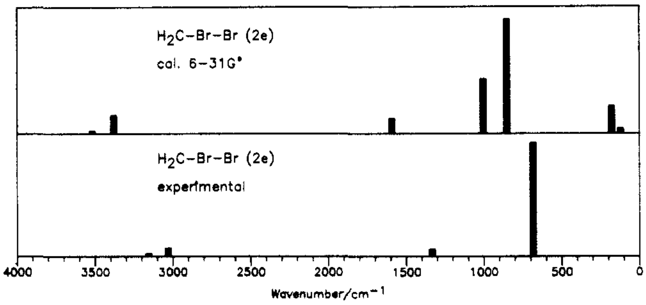


Figure 4. Comparison of the experimental and calculated IR spectrum of isodibromomethane (**2e**).

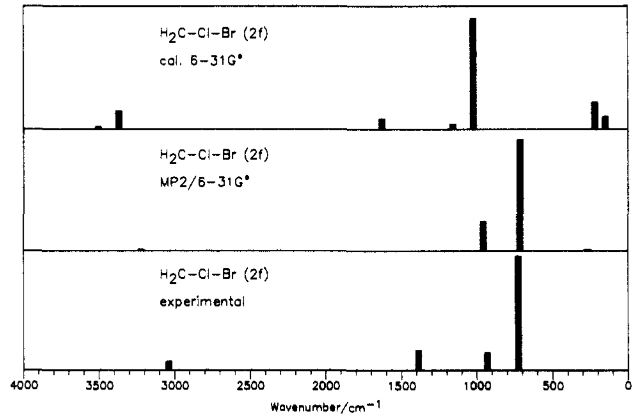


Figure 5. Comparison of the experimental and calculated IR spectrum of isobromochloromethane (**2f**).

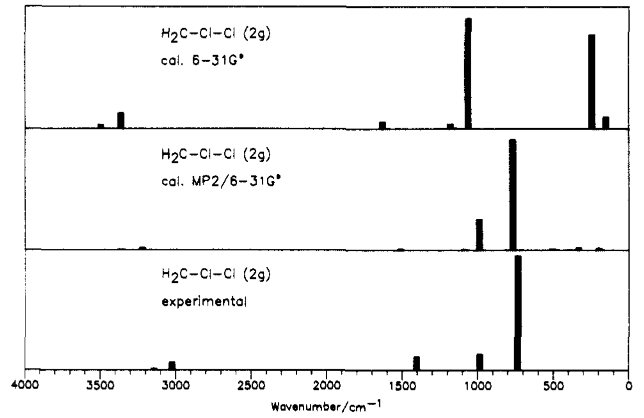


Figure 6. Comparison of the experimental and calculated IR spectrum of isodichloromethane (**2g**).

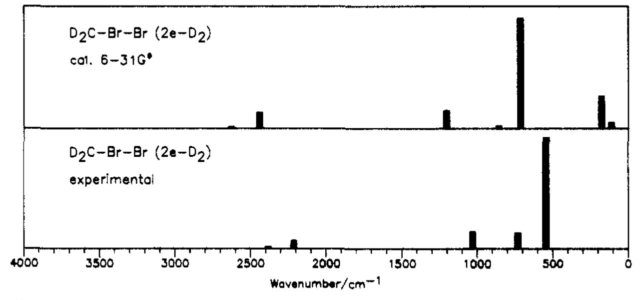


Figure 7. Comparison of the experimental and calculated IR spectrum of isodibromomethane (**2e**-d_2).

intense symmetrical mode should appear at lower frequency. Upon deuteration both bands are predicted to be shifted by about 20% to lower wavenumbers. This feature is found in the spectra of all isodihalomethanes, except for **2f**, where the signal to noise ratio is too low to observe the weak antisymmetric CH stretching band. The intensities of the CH stretching vibrations are much higher than the corresponding ones of precursors **1e–g**, which indicates

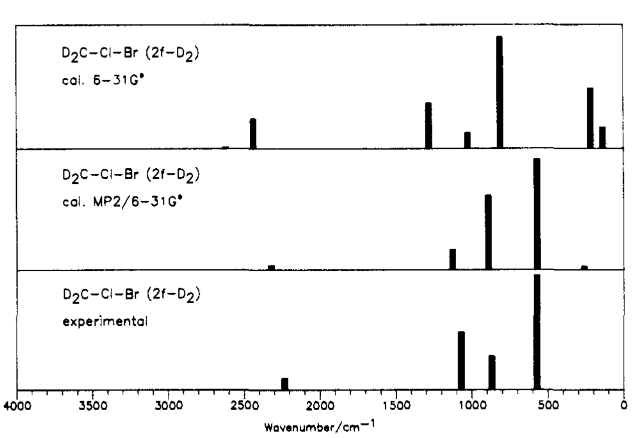


Figure 8. Comparison of the experimental and calculated IR spectrum of isobromochloromethane (**2f**-d_2).

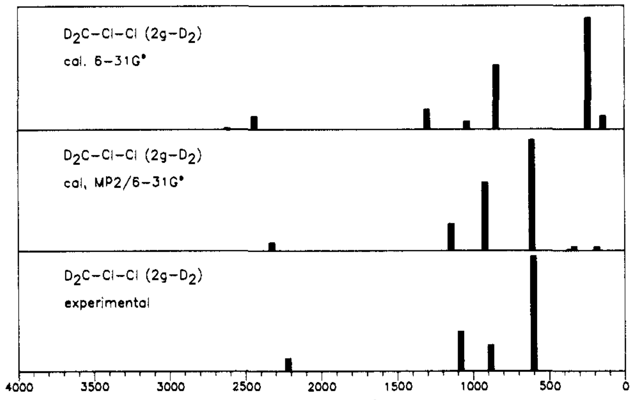


Figure 9. Comparison of the experimental and calculated IR spectrum of isodichloromethane (**2g**-d_2).

a higher polarity of the CH bonds according to the resonance structures **2A**, **2D**, and **2E**.

The CH_2 scissoring vibrations are calculated to appear as weak bands at 1591 (**2e**), 1628 (**2f**), and 1635 cm^{-1} (**2g**) at the 6-31G* level (Table III). Their deuterated counterparts should absorb at 1205 (**2e**-d_2), 1282 (**2f**-d_2), and 1300 cm^{-1} (**2g**-d_2) (Table IV). In good agreement with this prediction the experimental values are observed in the same order of frequency at 14–17% lower values (**2e**, 1334; **2f**, 1388; **2g**, 1405; **2e**-d_2, 1030; **2f**-d_2, 1070; **2g**-d_2, 1083 cm^{-1}). The rocking and twisting vibrations of the CH_2 group are predicted to have very low intensities and were not observed in the experimental spectra.

The calculated bands of highest intensity that, from the calculated normal modes, can be described as a CH_2 wagging vibration, weakly mixed with the C–X stretching, should appear at 853 (**2e**), 1023 (**2f**), and 1066 cm^{-1} (**2g**). The strongest bands of the experimental spectra are observed in the same ordering at 20–30% lower frequencies (**2e**, 684, **2f**, 727; **2g**, 763 cm^{-1}). The observed deuterium shift of −20% is also predicted well by the calculation (**2e**, −16%; **2f**,**g**, −21%). The frequency variation of this band with the halogen substituents Cl, Br, and I covers a range of 150 cm^{-1}. The lowest value is found for the diiodo derivative (**2a**, 611 cm^{-1}), and the highest, for the dichloro derivative (**2g**, 763 cm^{-1}). It is interesting to note that the influence of the terminal halogen atom is much more important than that of the halogen atom directly bound to the C atom. From **2a** to **2c** (variation of the central halogen) the wagging vibration is increased by only 30 cm^{-1}, whereas the change of the terminal halogen atom from I to Cl increases the frequency by 130 cm^{-1} (**2c**, **2f**, **2g**). A comparison of the CH_2 wagging vibrations with those of the corresponding matrix-isolated radicals ($CH_2Cl^\bullet$,[11a–c]

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[11] (a) Jacox, M. E.; Milligan, D. E. *J. Chem. Phys.* **1970**, *53*, 2688. (b) Andrews, L.; Smith, D. W. *J. Chem. Phys.* **1970**, *53*, 2956. (c) Michault, J. P.; Roncin, J. *Chem. Phys. Lett.* **1971**, *12*, 95.

Table III. Experimental IR Spectra (Ar Matrix, 12 K) of the Isodihalomethanes **2a–2c** and **2e–2g**

approx description	H_2CI–I (**2a**)	H_2CBr–I (**2b**)	H_2CCl–I (**2c**)	H_2CBr–Br (**2e**)	H_2CCl–Br (**2f**)	H_2CCl–Cl (**2g**)
CH_2 str	3151.2 (0.01)[b]	3165.2 (0.02)[b]	3168.8 (0.01)[b]	3156.3 (0.02)[b]		3143.3 (0.02)[b]
CH_2 str	3028.0 (0.03)	3040.3 (0.04) 3035.7 (0.08) 3030.9 (0.02)	3042.3 (0.24) 3039.4 (0.13)	3030.4 (0.07)	3038.6 (0.07) 3029.7 (0.03)	3030.4 (0.03) 3023.5 (0.08)
2 CX str			1760.5 (0.03) 1747.2 (0.01)			
CH_2 scis	1372.8 (0.05)			1346.0 (0.01) 1333.6 (0.06)	1388.3 (0.17) 1381.6 (0.03)	1407.8 (0.02) 1404.9 (0.08)
CX str + CH_2 wag	1291.3 (0.02)		1510.3 (0.01) 1503.5 (0.03)			1702.4 (0.02) 1695.9 (0.01)
2 CH_2 wag	1231.8 (0.01) 1260.6 (0.03)	1260.8 (0.05) 1247.3 (0.05)	1268.2 (0.06) 1261.0 (0.17)	1482.3 (0.02) 1463.8 (0.02)	1485.7 (0.06)	1561.6 (0.02) 1545.0 (0.08)
CX str	713.6 (0.04) 704.6 (0.07)		886.2 (0.56) 879.4 (0.23)[a]		931.2 (0.15) 924.5 (0.06)[a]	967.2 (0.01) 958.5 (0.12) 952.7 (0.02)[a]
CH_2 wag	622.7 (0.69) 618.3 (0.65) 616.2 (0.55) 611.1 (1.00)	640.5 (0.18) 638.1 (0.74) 630.6 (1.00) 629.2 (0.26)	639.0 (0.48) 633.5 (1.00)	695.2 (0.08) 684.4 (1.00)	726.6 (1.00) 717.4 (0.11)	772.6 (0.18) 763.2 (1.00)

[a] Isotopic splitting by ^{37}Cl. Other splittings are caused by matrix effects. [b] Intensities are in parentheses.

Table IV. Experimental IR Spectra (Ar Matrix, 12 K) of the Isodihalomethanes **2a**-d_2–**2c**-d_2 and **2e**-d_2–**2g**-d_2

approx description	D_2CI–I (**2a**-d_2)	D_2CBr–I (**2b**-d_2)	D_2CCl–I (**2c**-d_2)	D_2CBr–Br (**2e**-d_2)	D_2CCl–Br (**2f**-d_2)	D_2CCl–Cl (**2g**-d_2)
CD_2 str	2377.6 (0.03)[c]	2394 (0.01)[c] 2390.4 (0.02)	2395.2 (0.03)[c]	2384.1 (0.02)[c]		2375.5 (0.01)[c]
CD_2 str	2213.0 (0.08)	2219.3 (0.08) 2222.6 (0.12)	2228.2 (0.39)	2213.2 (0.07)	2232.3 (0.10) 2225.5 (0.04)	2227.0 (0.08) 2220.7 (0.17)
CD_2 scis	1040.7 (0.01) 1032.7 (0.04)	1054.9 (0.02) 1050.8 (0.02)	1072.5 (0.16)	1035.4 (0.02) 1029.8 (0.15)	1069.6 (0.56) 1005.3 (0.12)	1086.7 (0.26) 1083.4 (0.47)
2 $(CD)_2$ wag	968.3 (0.05) 952.9 (0.08)	990.8 (0.03) 986.2 (0.16) 976.8 (0.11)	987.4 (0.26)	1116.0 (0.01) 1102.6 (0.04)		1224.1 (0.03) 1210.6 (0.09)
CX str	645.3 (0.07)	713.6 (0.09) 712.4 (0.10)[b] 707.5 (0.12) 706.1 (0.12)[b] 701.0 (0.07) 699.6 (0.06)[b]	836.5 (0.96) 829.5 (0.38)[a]	732.4 (0.07) 730.9 (0.07)[b]	868.8 (0.29) 863.3 (0.11)[a]	891.5 (0.11) 886.1 (0.33) 879.4 (0.14)[a] 874.6 (0.04)
CD_2 wag	498.0 (0.49) 493.7 (0.21) 488.6 (1.00) 485.5 (0.25)	508.4 (0.23) 505.3 (1.00) 500.0 (0.80)	502.9 (0.48) 498.8 (1.00)	553.7 (0.18) 545.5 (1.00)	573.3 (1.00) 566.5 (0.27)	610.4 (0.35) 603.1 (1.00)

[a] Isotopic splitting caused by ^{37}Cl. [b] Isotopic splitting caused by ^{81}Br. Other splittings are caused by matrix effects. [c] Intensities are in parentheses.

402 cm^{-1}; $CH_2Br^{\bullet}$,[12a,b] 368 cm^{-1}; $CH_2I^{\bullet}$,[13] 375 cm^{-1}), which are more than 250 cm^{-1} lower, indicates that the isohalomethanes **2** are much "stiffer" than the radicals with respect to this kind of "umbrella" motion in accordance with the resonance structures **2C**/**E**.

The identification of the CCl stretching vibrations is easily made by considering the expected isotopic splitting by the ^{35}Cl and ^{37}Cl isotopes, which have natural abundances of 0.75 and 0.25. It turns out that the pairs of bands at 886.2/879.4 (**2c**), 931.2/924.5 (**2f**), and 958.5/952.7 cm^{-1} (**2g**), which are shifted by only 7–9% on deuteration, can be assigned to the CCl stretching vibrations. The observed isotopic shifts of about 6–7 cm^{-1} are confirmed by the calculations for **2f** and **2g** (calculated 7.9 cm^{-1}). (Even a rough estimation of the $^{35}Cl/^{37}Cl$ shift by Hook's law for the diatomic C–Cl oscillator matches the observed values.)

Because of their low intensities the assignments of the CI and CBr stretching bands are more difficult. Weak bands at 705 (**2a**) and 645 cm^{-1} (**2a**–d_2) may arise from CI stretching vibrations. Absorptions that are probably due to CBr stretching vibrations can only be observed for the deuterated compounds **2b**–d_2 (around 710 cm^{-1}) and for **2e**–d_2 (730 cm^{-1}). In addition to some disturbances by matrix effects, they show the expected $^{79}Br/^{81}Br$ isotopic splitting of 1.5 cm^{-1}.

Table V. CCl Stretching Frequencies of Chloromethane Derivatives[a]

Y–CH_2–Cl	$CH_2Cl^{\bullet}$[b]	CH_2Cl–Y	CH_2Cl^{+}[c]
746 (**1g**)		959 (**2g**)	
745 (**1f**)	827	931 (**2f**)	1040
735 (**1c**)		886 (**2c**)	

[a] Frequencies in reciprocal centimeters. [b] Reference 11. [c] Reference 14.

Table V gives a comparison of the CCl stretching frequencies of the isodihalomethanes **2c**, **2f**, and **2g** with other chloromethyl derivatives. The fact that bands for **2c**, **2f**, and **2g** are found at higher wavenumbers than for the tetrahedral precursors **1c**, **1f**, and **1g** ("normal" CCl single bond) and the chloromethyl radical[11] indicates that the CCl bond order in **2c**, **2f**, and **2g** is considerably higher than 1. This corresponds well with the calculated C–Cl bond lengths (**2f**, 1.579 Å; **2g**, 1.571 Å), which are shorter than normal C–Cl single bonds (**1f**, 1.756 Å; **1g**, 1.768 Å). On this basis the resonance structures **2B** for a weak carbene–halogen charge-transfer complex and also the radical pair type resonance structures **2F**/**2G** seem rather unimportant. On the other hand, both resonance structures **2C** and **2E** can account for the calculated and observed bond shortening. In this context it may be mentioned that a decision between an halonium-ylide type (**2A**) and an

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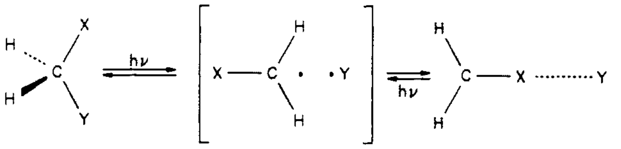
[12] (a) Smith, D. W.; Andrews, L. *J. Chem. Phys.* **1971**, *55*, 5295. (b) Andrews, L.; Miller, J. H.; Prochaska, E. S. *J. Am. Chem. Soc.* **1979**, *101*, 7158.

[13] Smith, D. W.; Andrews, L. *J. Chem. Phys.* **1973**, *58*, 5222.

ion-pair type structure (**2D** ↔ **2E**) is provided by the calculated atomic charges that favor the latter. Only the C–Cl stretching vibration of the CH_2Cl^+ cation in the gas phase (1040 cm^{-1}) is found at a higher wavenumber.[14] This means, if the resonance structures **2D** ↔ **2E** corresponding to an ion pair contribute primarily to the actual structure, an interaction between the central and the terminal halogen atoms, which weakens the C–X bond with respect to the free halocarbenium–ion, has to be taken into account as well. Indeed, a characteristic decrease of the CCl stretching frequencies is observed if the polarizability of the terminal halogen atom increases (see Table III). The calculated structures of **2e**, **2f**, and **2g** show definite, but weak, bonds between the halogen atoms. The bond lengths (**2e**, 2.823 Å; **2f**, 2.734 Å; **2g**, 2.576 Å) are much larger than those of the corresponding diatomic molecules (Br_2, 2.290 Å; BrCl, 2.138 Å; Cl_2, 1.988 Å; experimental values). Unfortunately, the X–Y stretching vibration cannot be observed in the experimental IR spectra. Following the predictions of the calculations, one can expect that they probably lie beyond the lower frequency limit of our spectrometer (220 cm^{-1}) and may be rather weak. The same is true for the CXY bending vibrations, which are expected to appear at even lower frequencies. Accordingly, none of these bands can be observed experimentally.

Mechanism. If two different halogen atoms are present (**1b**, **1c**, and **1f**), it is the heavier one that migrates. A mechanism that assumes a homolytic cleavage of the weaker one of the two carbon halogen bonds (C–Y) as the primary step can explain the selectivity of the reaction. The same selectivity is observed in the gas-phase photolysis of bromoiodomethane (**2b**).[15]



1 *3* *2*

The radical pair **3** cannot dissociate in the solid matrix, in contrast to the gas phase, and collapses either to the educts **1** or to the products **2**. The formation of the isomers **2** was unexpected, but comparable addition reactions of free fluorine atoms to the halogen atoms of matrix-isolated methyl halides are well-known.[16]

The photoisomerizations described are not restricted to dihalomethanes. We have investigated the photochemistry of other matrix-isolated halomethanes[17] and observed the same kind of reaction for the trihalomethane $CHBrCl_2$ and the tetrahalomethanes CCl_3I, CI_4, CBr_4, and CCl_4. With the aid of the calculated IR spectrum we were able to assign the observed bands of isotetrachloromethane to six of the nine fundamental vibrations[6b] and to simulate their pattern of $^{35}Cl/^{37}Cl$ isotopic splitting.

We believe that the isomers **2** play an important part in the photo- and radiochemistry[18] of all halomethanes. They should be considered whenever such irradiation is carried out in the solid or liquid state.

Table VI. Optimized Conditions for the Photolysis **1** → **2**

precursor	wavelength (nm)	irrad. time (min)	conversion (%)
1a	313^a	3	30
1b	300^a	40	25
1c	300^a	240	30
1e	240^b	60	10
1f	230^b	240	7
1g	185^c	480	10

[a] HBO 200, monochromator. [b] XBO 450, monochromator. [c] Hg low-pressure lamp, interference filter.

V. Experimental Section

Chemicals. CH_2I_2, CH_2ClI, CH_2Br_2, CD_2Br_2, CH_2BrCl, CBr_4, $CBrCl_3$, and CCl_4 were commercially available and were used without further purification. CD_2I_2 was prepared from CD_2N_2 and iodine and purified by preparative GC. CH_2BrI and CD_2BrI were obtained by stirring CH_2Br_2 or CD_2Br_2 and an aqueous solution of NaI in the presence of tetrabutylammonium chloride and subsequent preparative GC. CD_2ClI was prepared in the same way starting from CD_2Cl_2. CH_2FI was obtained from the reaction of CH_2I_2 with solid HgF_2[19] and preparative GC; CD_2BrCl was prepared from CD_2Cl_2 and solid $AlBr_3$, followed by preparative GC.

Matrix isolation equipment: Displex closed cycle system CSA 202, Air Products, with CsI (IR) and BaF_2 (UV/vis) windows.

Photochemical equipment: Hg super-high-pressure lamp, Model HBO 200 (Osram), with a monochromator (Bausch & Lomb), Xe high-pressure lamp, Model XBO 450 (Osram), with a monochromator (Beckman), Hg low-pressure lamp, Flächenstrahler (Gräntzel), with interference filters at 254 and 185 nm, excimer laser LPX 100 (Lambda Physik).

Spectrometer: FT-IR IFS 85 (Bruker), UV/vis Acta MVII (Beckman). The IR spectra were taken between 4000 and 220 cm^{-1} with 1-cm^{-1} resolution.

General Procedure for Sample Preparation and Photolysis. Gas mixtures of the halomethanes and argon (molar ratio 1:1000) were prepared by vacuum line techniques with standard manometric equipment. About 5 mmol of the gas mixture was condensed onto a CsI or BaF_2 window, held at 12 K, and photolyzed. The progress of the reaction was monitored by IR and/or UV/vis spectroscopy. For each halomethane, the wavelength and the irradiation time were optimized in order to obtain a maximum of interconversion **1** → **2** and a minimum of side reactions (Table VI). The backward reaction **2** → **1** was achieved by using white light or monochromatic light according to the absorption maxima of **2**. It was important to shield the samples from daylight during the experiments. It was impossible to record the IR spectra with a grating spectrometer, for the light emitted by the Nernst glower destroyed the isomers **2** within minutes.

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Registry No. **1a**, 75-11-6; **1b**, 557-68-6; **1c**, 593-71-5; **1d**, 373-53-5; **1e**, 74-95-3; **1f**, 74-97-5; **1g**, 75-09-2; I^-, 20461-54-5; Br^-, 24959-67-9; Cl^-, 16887-00-6; H_2C^+I, 80371-47-7; H_2C^+Br, 70022-19-4; H_2C^+Cl, 59000-00-9; H_2C^+F, 35310-31-7.

Supplementary Material Available: Tables of calculated infrared frequencies and intensities (2 pages). Ordering information is given on any current masthead page.

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(14) (a) Andrews, L.; Dyke, J. M.; Jonathan, N.; Keddar, N.; Morris, A.; Ridha, A. *Chem. Phys. Lett.* **1983**, *87*, 89. (b) Andrews, L.; Dyke, J. M.; Jonathan, N.; Keddar, N.; Morris. A. *J. Phys. Chem.* **1984**, *88*, 1950.

(15) Lee, S. J.; Bersohn, R. *J. Phys. Chem.* **1982**, *86*, 728.

(16) Jacox, M. E. *J. Phys. Chem.* **1985**, *83*, 3255; *Chem. Phys.* **1980**, *51*, 69.

(17) Maier, G.; Reisenauer, H. P. Unpublished results.

(18) Radiolysis of CCl_4: Bühler, R. E. *Radiat. Phys. Chem.* **1983**, *21*, 139. Radical cations of CCl_4: Drewello, T.; Weiske, T.; Schwarz, H. *Angew. Chem.* **1985**, *97*, 855; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 869. Theoretical study of *i*-CCl_4: Reed, A. E.; Weinhold, F.; Weiss, R.; Macheleid, J. *J. Phys. Chem.* **1985**, *89*, 2688.

(19) Burton, D. J.; Greenlimb, P. E. *J. Org. Chem.* **1975**, *40*, 2796.