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Citation: The Journal of Chemical Physics **41**, 3032 (1964); doi: 10.1063/1.1725669 View online: http://dx.doi.org/10.1063/1.1725669 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/41/10?ver=pdfcov Published by the AIP Publishing

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 O_2 is the same as O_1 except for a reversal of the positive and negative signs. Thus, like the case of a singlet state, it is possible to place the important elements H_{-11} and H'_{-11} on the main diagonal. It will be noted that in O_1 the *c* levels of the F_1 component (upper left submatrix) are mixed with the d level of the F_2 component (lower right submatrix). Similarly in O_2 the d levels of the F_1 component are mixed with the *c* levels of the F_2 component. Similar conclusions apply to the

 E_1 and E_2 submatrices which can be obtained from E by using the modified Wang matrix W.

For triplet states the same procedure may be carried through with the aid of the transformation matrix,

$$W^{-1} = W = \text{diag.}(X, X', X''),$$
 (AII.4)

where X, X', and X'' are Wang matrices of appropriate order.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 41, NUMBER 10

15 NOVEMBER 1964

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HCO and DCO have been prepared by the photolysis of HI (DI) and of H_2S (D₂S) in a CO matrix at 14° and at 20°K. The earlier infrared spectroscopic identification of these species has been confirmed. The C=O stretching frequency of DCO has been revised to 1800 cm⁻¹. Unusually low C-H and C-D stretching frequencies, 2488 and 1937 cm⁻¹, respectively, are obtained. Observations on H13CO and D13CO support these assignments. Spectroscopic, kinetic, and electron spin resonance data all suggest that the C-H bond is exceptionally weak. Fermi resonance may occur between the C-D and C=O stretching modes of DCO. Evidence is presented suggesting that considerable activation energy is required for the reaction of H atoms with CO.

INTRODUCTION

THE first spectroscopic studies of the reaction inter-mediate HCO were those of $Ramsay^1$ and of Herzberg and Ramsay,² who conducted high-resolution studies of the 7500-4500-Å absorption system of this species. The electronic transition was found to involve the ground state, in which HCO is bent, and an excited state in which the species is linear. The production of the HCO absorptions in considerably greater intensity by Johns, Priddle, and Ramsay³ has led to a clarification of several details of the earlier assignment. These workers have established that the electronic transition is ${}^{2}A''\Pi - {}^{2}A'$, in agreement with the predictions of Walsh.⁴ Most of the vibrational frequencies of the upper $({}^{2}A''\Pi)$ states of HCO and DCO have been determined from these observations. The ground-state $(^{2}A')$ bending vibration has been found to be 1083.0 cm⁻¹ for HCO and 847.4 cm⁻¹ for DCO.

Direct infrared spectroscopic observations of HCO and DCO have been made by Ewing, Thompson, and Pimentel,⁵ who produced these species by the reaction of photolytically produced H(D) atoms with a CO matrix at 20°K. Two fundamentals of HCO and, as is shown, one of DCO were observed by these workers. Arguments were presented indicating that the C=O stretching frequency of DCO lies very close to that of HCO. Ewing, Thompson, and Pimentel were unable to assign frequencies to the C-H and C-D stretching modes of HCO and DCO.

In an attempt to determine whether several photolytic processes involve the production of H atoms, it was decided to observe the products of photolysis of the species of interest suspended in a CO matrix. The first substance to receive such study, H₂S, was found to yield considerably more intense absorptions due to HCO than had previously been observed. With such greatly enhanced concentrations of HCO, it was hoped that further study might yield a positive identification of the C-H and C-D stretching frequencies, as well as to confirm the assignment of the C=O stretching frequency of DCO. As is seen, all of these expectations have been realized.

EXPERIMENTAL TECHNIQUES

H₂S and HI were used as sources of H atoms in the present experiments. D₂S was prepared by repeated isotopic exchange between H₂S and D₂O. DI was prepared by the reaction of D₃PO₄ with KI. Gaseous mixtures of these substances with CO were prepared by

¹D. A. Ramsay, J. Chem. Phys. 21, 960 (1953). ²G. Herzberg and D. A. Ramsay, Proc. Roy. Soc. (London) A233, 34 (1955). ³J. W. C. Johns, S. H. Priddle, and D. A. Ramsay, Discussions Faraday Soc. No. 35, 90 (1963). ⁴A. D. Walsh, J. Chem. Soc. 1953, 2292. ⁵G. E. Ewing, W. E. Thompson, and G. C. Pimentel, J. Chem. Phys. 32, 927 (1960).

standard manometric techniques. In most of the experiments the CO: (H atom source) mole ratio was approximately 100. In some experiments, the CO was enriched to 56.5%¹³CO.

The cryostat used in these experiments is similar to that described by Milligan.⁶

Observations were made at 14° and at 20°K, the triple point and the normal boiling point of hydrogen, respectively.

After the pattern of the initial and the product absorptions had been established, it was possible to enhance the intensity of the HCO (DCO) absorptions by conducting deposition and photolysis simultaneously. Photolysis was by direct irradiation through a barium fluoride or a sodium chloride window, using a mediumpressure mercury arc and a quartz focusing lens.

Infrared spectra were recorded on a double-beam prism-grating spectrometer (Beckman IR-9). Under the conditions of a typical experiment, the resolution is approximately 1 cm⁻¹ throughout the spectral range studied. The absolute frequency accuracy is approximately ± 1 cm⁻¹ between 400 and 2000 cm⁻¹ and ± 2 cm⁻¹ between 2000 and 4000 cm⁻¹.

OBSERVATIONS

Spectral features of the various isotopic species of formaldehyde appear during photolysis and grow in intensity throughout the period of irradiation. When H_2S or D_2S is used as a source of H (D) atoms, the infrared absorptions of OCS, but not of CS₂, also appear. The remaining product absorptions in typical experiments are illustrated in Figs. 1–3. Even with the excellent yield of HCO of the experiment shown in Fig. 1, no new absorptions, except those due to H_2CO , were



observed above 2500 cm⁻¹. The intensity of the 1861cm⁻¹ HCO absorption is so great in this experiment that the 1821-cm⁻¹ H¹³CO absorption, contributed by the 1% natural abundance of this species, can be detected. In Fig. 2, the two traces, showing the absorptions in the CO:DI system before and after prolonged photolysis, have been vertically displaced for clarity. It is evident that all of the absorptions shown in this trace slowly diminish in intensity on prolonged photolysis. There is a corresponding growth in the absorptions assigned to D₂CO and to HDCO. Figure 3, illustrating a 56% ¹³CO:DI experiment, also shows a background peak at 2505 cm⁻¹, possibly contributed by a small



⁶ D. E. Milligan, J. Chem. Phys. 35, 1491 (1961).

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FIG. 3. CO $(56\% \ ^{13}CO)$: DI=50. 14°K. 98 mm×2 liter, deposited with simultaneous photolysis over period of 175 min.

amount of HBr, and a broad background absorption near 1795 cm⁻¹, possibly due to DBr impurity. The frequencies corresponding to the absorptions shown in Figs. 1–3 are summarized in Tables I and II.

The relative intensities of the sets of three product peaks are independent of the source of H (D) atoms and, within the limits of the present observations, of the mole ratio, duration of photolysis, and temperature. The 1861-cm⁻¹ absorption in the H+CO experiments has approximately three times the optical density of the 1090-cm⁻¹ absorption (in contrast to the 1:1 ratio reported for HCO by Ewing, Thompson, and Pimentel) and 10 times the optical density of the 2488-cm⁻¹ absorption. The broad 2488-cm⁻¹ absorption does not appear to split when a 56.5% 13CO matrix is employed, but undergoes further broadening, so that the sum of the optical densities of the 1821- and 1861-cm⁻¹ peaks is approximately 14 times the optical density calculated from the peak intensity of the 2488-cm⁻¹ absorption. This behavior is to be anticipated if the 2488-cm⁻¹ peak has an unresolved splitting in the 56.5% ¹³CO matrix experiments.

All of the absorptions listed in Tables I and II have been found to disappear at a temperature of approximately 35°K, before loss of the CO film from the cold window. Indeed, in many of the experiments having relatively high intensities of these absorptions, once the sample had started to warm the temperature of

 $\begin{array}{c} {\rm T}_{\rm ABLE} \ I. \ {\rm Absorptions} \ (reciprocal \ centimeters) \ appearing \\ {\rm following \ photolysis \ of \ HI \ or \ H_2S \ in \ CO.} \end{array}$

12CO matrix	56.5% ¹³ CO matrix	
 	1084	
1090	1090	
	1821	
1861	1861	
2488	2488	

the film rose so rapidly that it was not possible to recool the window before the sample was lost from it. Such behavior, of course, indicates the presence of a highly reactive species. Observations of the deposit after warmup and recooling gave no evidence for the production of glyoxal or other new species.

DISCUSSION

Vibrational Assignment of HCO

The constant relative intensities of the 2488-, 1861-, and 1090-cm⁻¹ absorptions, their simultaneous disappearance upon warmup, and the tendency of all of them to diminish in intensity upon prolonged photolysis suggest that all three of these absorptions are contributed by HCO. The observations on H¹³CO are consistent with this hypothesis. The behavior of the 1937-, 1800-, and 852-cm⁻¹ bands also suggests that DCO is responsible for all three of them.

The C=O stretching frequency of DCO had previously been assigned at 1860 cm^{-1} by Ewing, Thompson, and

TABLE II. Absorptions (reciprocal centimeters) appearing following photolysis of DI or D₂S in CO.

¹² CO matrix	56.5% ¹³ CO matrix	
	845	
852	852	
	1780	
1800	1800	
	1910	
1937	1938	

Pimentel. The present experiments leave no doubt that the correct value should be 1800 cm^{-1} . Possibly in the earlier work this absorption was masked by DBr impurity; the 1800 cm^{-1} absorption is considerably less intense than its 1861-cm^{-1} counterpart. The photometric argument of the earlier workers leading to the assignment of the C=O stretching frequencies of both DCO and HCO at 1860 cm^{-1} appears to be in error; in all of our experiments, regardless of deuterium content, the relative intensity of the 1861-cm^{-1} HCO absorption is approximately three times that of the 1090-cm^{-1} absorption.

Assuming, for the moment, that the 2488-cm⁻¹ absorption is contributed by the C-H stretching mode of HCO, it would be anticipated that the C-D stretching mode would fall in the 1800–1900-cm⁻¹ region. Thus, it would be possible for Fermi resonance interaction to occur between the C-D and the C=O stretching modes. The absorptions observed in the CO+D experiments are consistent with this possibility. The 1937-cm⁻¹ absorption, like the 2488-cm⁻¹ band in the H+CO system, is broad. The 1937-cm⁻¹ peak is, however, considerably more intense than the 2488-cm⁻¹ absorp

tion. On the other hand, the relative intensity of the 1800-cm⁻¹ absorption in the deuterated system is considerably less than that of the 1861-cm⁻¹ absorption. This behavior would be anticipated were Fermi resonance to occur; the C-D stretching mode would be expected to "borrow" intensity from the C=O stretching mode. The behavior of the system D+13CO parallels that of $D+^{12}CO$, and is consistent with the hypothesis of Fermi resonance.

The revised band assignment of Johns, Priddle, and Ramsay³ has yielded $T'_{000}(\text{HCO}) - T'_{000}(\text{DCO}) = +133$ cm⁻¹. The present assignment of all of the ground-state fundamentals of HCO and DCO permits the calculation of $\Delta T'_{000} = +171$ cm⁻¹. According to Johns, Priddle, and Ramsay, an error of approximately 10 cm⁻¹ is reasonable for their extrapolations. The sum of small matrix shifts may account for the remainder of the discrepancy. With several assumptions, Johns, Priddle, and Ramsay were able to estimate a ground-state C-H stretching frequency of 2700±100 cm⁻¹. Despite the large error involved in this estimate, it does suggest that the C-H stretching frequency may lie somewhat lower than that in more typical species.

The reluctance of Ewing, Thompson, and Pimentel to assign the 2488- and 1937-cm⁻¹ absorptions, which they also observed, to the C-H and C-D stretching modes of HCO and DCO, respectively, is certainly understandable. On the other hand, HCO is hardly a typical molecule. Indeed, the assignment of a C=O stretch at 1860 cm⁻¹ is also outside the usual range for such a mode. Considerable uncertainty remains regarding the value of the C-H dissociation energy of this species. Klein and Schoen^{7,8} have given this dissociation energy a lower bound of 27 kcal/mole, based on their observations of the gas-phase photolysis of H_2CO . It is noteworthy that they have estimated a strength of approximately 78 kcal/mole for the first C-H bond of H₂CO. Earlier work by Calvert et al.⁹⁻¹¹ had suggested an H-CO dissociation energy as low as 14 kcal/mole. This value, however, was derived subject to assumptions regarding the mechanism of photolysis of H₂CO. From

TABLE III. Force constants for HCO.

Approxi- mation	Frequencies used for calculation	k _{CH} (mdyn/Å)	k _{CO} (mdyn/Å)	k _{HCO} (mdyn∙Å)
A B C	1090, 1861, 2488 1090, 1861 1861, 2488	3.32 3.32	$14.07 \\ 13.90 \\ 14.34$	0.675 0.674

⁷ R. Klein and L. J. Schoen, J. Chem. Phys. **24**, 1094 (1956). ⁸ R. Klein and L. J. Schoen, J. Chem. Phys. **29**, 953 (1958). ⁹ F. E. Blacet and J. G. Calvert, J. Am. Chem. Soc. **73**, 661 (1951).

¹⁰ J. G. Calvert and E. W. R. Steacie, J. Chem. Phys. 19, 176 (1951).

TABLE IV. Absorptions (reciprocal centimeters) for H13CO.

Approximation	C-H stretch	C=O stretch	HCO bend
B C observed	2478 <2488	1819 1823 1821	1085 1084

their observation of the predissociation of HCO, Johns, Priddle, and Ramsay³ have established an upper bound of 35.4 kcal/mole for the dissociation energy of HCO.

Independent evidence for the weakness of the C-H bond of HCO has been provided by the electron-spinresonance study of this species by Adrian, Cochran, and Bowers.¹² These workers have found an exceptionally large isotropic proton hyperfine splitting for HCO. They have suggested that this splitting may be explained by configuration interaction between the ground state and a low-energy excited state consistent essentially of an unbonded H atom interacting with a CO molecule.

With this identification of the C-H stretching frequency of HCO, it becomes possible to solve the secular determinant for all three of the valence force constants of this species. The values of the three frequencies are such that the approximate separation of any one of them is not entirely satisfactory. By choosing values for the C-H force constant and solving the resulting quadratic equation for the remaining two force constants, the set given in Table III as Approximation A has been found to be consistent with the observed data. Approximate separation of the two lower frequencies (Approximation B) or of the two higher frequencies (Approximation C) yields values for the various force constants in reasonable agreement with the more exact values obtained by the successive approximation procedure. It must be noted that these force-constant calculations have required the use of the molecular dimensions derived by Johns, Priddle, and Ramsay³ from their observed moments of inertia assuming that the C-H bond distance is 1.08 Å. In view of the atypical C-H stretching frequency and force constant for HCO, there may be an appreciable deviation from this bond length. Nevertheless, it should be anticipated that the frequencies calculated from these force constants for H¹³CO, in which the mass perturbation is relatively small, should agree reasonably well with the experimentally observed frequencies. As is shown by Table IV, the agreement is indeed quite good.

It is noteworthy that the C-H stretching force constant is relatively small, while the C=O force constant is relatively large. Its value, 14.1 mdyn/Å, is intermediate between that of $H_2C=O(12.3 \text{ mdyn/Å})$ and that of C=O (18.6 mdyn/Å). Such values for the stretching force constants of HCO are consistent with

¹¹ J. G. Calvert, J. Chem. Phys. 29, 954 (1958).

¹² F. J. Adrian, E. L. Cochran, and V. A. Bowers, J. Chem. Phys. 36, 1661 (1962).

the configuration interaction postulated by Adrian, Cochran, and Bowers.¹²

Because small errors in the structural parameters are very important for such large perturbations as that of substituting a D atom, and because the anharmonic contribution to the C-H (C-D) stretching mode of HCO (DCO) is expected to be unusually large, the prediction of DCO frequencies from HCO force constants is relatively unsatisfactory. A check based upon observable quantities is provided by the familiar product-rule calculations. Using the ground-state moments of inertia observed by Johns, Priddle, and Ramsay for HCO and DCO and substituting all of the observed fundamentals of these species except the C-D stretching frequency, the stretching frequency calculated for DCO is 1861 cm⁻¹. This value is sufficiently close to the frequency observed for the C=O stretching mode to indicate that Fermi resonance may occur. The complications of Fermi resonance and unusually large anharmonicity quite conceivably could combine to raise the observed C-D stretching frequency as high as 1937 cm⁻¹.

Mechanism of the Photolytic Reaction

Geib and Harteck,¹³ using chemical methods of detection, found no evidence for reaction between H atoms generated in a discharge and CO at 83°K. As has been suggested by Ewing, Thompson, and Pimentel,⁵ Geib and Harteck's failure to observe a reaction could be accounted for by a requirement that H atoms have an appreciable activation energy for reaction with HCO or by the occurrence of the reaction

$$H + HCO \rightarrow H_2 + CO.$$
(1)

In the present experiments, appreciable quantities of H_2CO have been observed. The concentration of this species has been observed to grow continuously during the course of photolysis, apparently at the expense of HCO upon prolonged photolysis. The growth of H_2CO is also noted in experiments in which HI is the source of H atoms. In this system, the iodine produced serves to filter much of the more energetic radiation which would be required for the production of H_2^* or CO^{*}. Although such processes as a three-body reaction of two H atoms with CO cannot be excluded as a source

¹³ K. H. Geib and P. Harteck, Chem. Ber. 66B, 1815 (1933).

of at least some of the H_2CO , it appears likely that Reaction (2) is the major source of this species:

$$H+HCO\rightarrow H_2CO.$$
 (2)

Thus, it appears quite likely that only relatively energetic H atoms may react with CO to produce HCO.

Further evidence suggesting that this is indeed the situation has been provided by attempts to produce HCO by the reaction of H atoms with CO in an Ar matrix. Under conditions comparable to those in which H atoms have been observed¹⁴ to react with O_2 to produce an appreciable yield of HO₂, no HCO has been detected spectroscopically. It would be anticipated that in an Ar matrix most of the H atoms would be reduced to thermal energies before encountering CO molecules.

When H_2S is used as the source of H atoms, OCS is also produced. In ultraviolet observations of the photolysis products of H_2S in an Ar matrix,¹⁵ the species SH and S_2 have been detected. These species have not been detected in the corresponding observations on H_2S photolyzed in a CO matrix. Therefore, such reactions as (3) and (4) must occur in this system:

$$SH+CO\rightarrow OCS+H$$
, (3)

$$S+CO\rightarrow OCS.$$
 (4)

CONCLUSIONS

The infrared spectroscopic observation of HCO by Ewing, Thompson, and Pimentel⁵ has been confirmed. The C=O stretching frequency of DCO has been revised to 1800 cm⁻¹, and the C-H and C-D stretching frequencies of HCO and DCO have been identified at 2488 and 1937 cm⁻¹, respectively. The corresponding frequencies of H¹³CO and D¹³CO have also been obtained. Fermi resonance may occur between the two stretching modes of DCO. It appears likely that considerable activation energy is required for the reaction of H atoms with CO.

ACKNOWLEDGMENT

We are deeply grateful to Dr. John T. Yates for making available to us the sample enriched to 56.5% ¹³CO.

¹⁴ D. E. Milligan and M. E. Jacox, J. Chem. Phys. **38**, 2627 (1963).

¹⁵ D. E. Milligan and M. E. Jacox (to be published).