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Author

Schaefer III., Henry F.

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Mark R. Hoffmann and Henry F. Schaefer III

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Hydroxycarbene (HCOH) and Protonated Formaldehyde:
Two Potentially Observable Interstellar Molecules

Mark R. Hoffmann and Henry F. Schaefer III

Department of Chemistry and Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract

It is known that the lowest energy isomer of protonated formaldehyde has the proton attached to the oxygen atom, i.e., $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C} - \text{O} - \text{H}^+ \\ \diagup \\ \text{H} \end{array}$. Therefore, a purely statistical argument would suggest that the hydroxycarbene molecule HCOH is twice as likely as formaldehyde to be formed from H_3CO^+ via dissociative recombination, a process generally considered to be very important in interstellar clouds. Theoretical studies show that while HCOH has never been observed in the laboratory, it should nevertheless be a relatively stable molecule. Theoretical equilibrium structures for H_3CO^+ and HCOH suggest that they may be observed at 63.5 and 68.4 GHz, respectively.

Subject headings: interstellar: molecules - line identifications -
molecular processes

The discovery of interstellar formaldehyde in 1969 by Snyder, Buhl, Zuckerman, and Palmer represented the first identification of a polyatomic organic molecule in the interstellar medium. Although many larger organic molecules have since been detected, formaldehyde has been observed in at least 28 interstellar sources, is apparently the most widespread tetraatomic interstellar molecule, and continues to attract much astrophysical attention (Mann and Williams, 1980). Most models of the role of formaldehyde in interstellar clouds concur (Herbst and Klemperer, 1973; Watson, 1976; Mitchell, et al., 1978; Prasad and Huntress, 1980) that one of its most important reactions is

Since the pure rotational spectrum of H_3CO^+ has never been observed, one purpose of the present research was to predict the frequency of the prominent microwave spectral feature. Secondly we emphasize here (see also Green and Herbst, 1979) that H_3CO^+ should react further to yield the formaldehyde isomer HCOH , which has never been identified in the laboratory but may be observable in the interstellar medium.

There are a number of isomeric forms of H_3CO^+ , protonated formaldehyde, and it is reasonable to assume that the lowest energy isomer is the one which the interstellar modeling (Mitchell, et al., 1978; Prasad and Huntress, 1980) predicts to have a substantial abundance. Among these H_3CO^+ structures, the oxygen protonated geometry

has been established by previous theoretical studies (Haney, et al., 1970; Dill, et al., 1979; Nobes, et al., 1980) to lie lowest energetically. One of the purposes of the present paper is to pursue the idea that this theoretical finding has important implications for the dissociative recombination reaction of (2). This is seen most clearly by noting that dissociative recombination (Herbst and Klemperer, 1973) of the other low-lying H_3CO^+ isomer, in which all three hydrogen atoms are bonded to the C atom,

leads exclusively to formaldehyde.

One of the products of the dissociative recombination of (2) will also be formaldehyde. However, assuming a purely statistical distribution of reaction products one predicts equal numbers of the three products

Neither cis (4a) or trans (4b) hydroxycarbene has been identified

spectroscopically via laboratory experiments to date. However, these species have been very carefully characterized theoretically (Lucchese and Schaefer, 1978; Goddard, Yamaguchi, and Schaefer, 1981) and are both well defined minima on the H_2CO potential energy hypersurface. The trans form of HCOH lies ~ 5 kcal below the cis, and the barrier for isomerization of the former to formaldehyde is substantial, ~ 30 kcal.

Our contention is that, following Green and Herbst (1979), cis and trans hydroxycarbene are indeed formed in significant quantities in interstellar clouds via reaction (4). However, whether these species live long enough to be detected by radioastronomers depends to some degree on the exothermicities of reactions (4a) and (4b). The theoretical methods described briefly below suggest an exothermicity of 81 kcal for the formation of the lower-lying trans HCOH . This exothermicity is clearly in excess of the 30 kcal barrier for isomerization to formaldehyde. However, the HNC molecule has a comparable barrier for isomerization (Pearson, et al., 1975) to the lower energy HCN , and is apparently (Watson, 1974) formed via a similar dissociative recombination [with exothermicity of ~ 125 kcal (Allen, et al., 1980)], yet is observed in the interstellar medium (Snyder and Buhl, 1971). Therefore it seems likely that HCOH will at least occasionally decay to its ground vibrational state via infrared emission and live indefinitely thereafter (for HCOH tunneling lifetimes, see Gray, et al., 1981). This conclusion is consistent with the hypothesis that neutral fragments of ion-molecule reactions may be formed with large amounts of translational energy.

To provide an idea of the frequencies at which cis and trans HCOH and protonated formaldehyde might be observed in interstellar clouds, theoretical predictions of their molecular structures have been made. The self-consistent-field (SCF) level of theory was used in conjunction

with a double zeta plus polarization (DZ+P) basis set of contracted gaussian functions (Dunning, 1970). The resulting theoretical structures are summarized in the Figure.

Of particular interest for the interstellar problem is the comparison between the structures of H_3CO^+ and the two HCOH isomers, since large differences would suggest that a significant fraction of the exothermicity in reactions (4a) and (4b) would be channeled into vibrational energy of the product HCOH. This sort of a partitioning of the exothermicity would enhance the likelihood of the $\text{HCOH} \rightarrow \text{H}_2\text{CO}$ isomerization, and accordingly decrease the interstellar abundance of HCOH. However the HCOH fragment within H_3CO^+ has a structure not too terribly different from that of the isolated cis and trans isomers. The largest difference lies in the CO distance which is $\sim 0.07 \text{ \AA}$ shorter for H_3CO^+ . Nevertheless, this bond distance change considerably exceeds the C-N separation change of $0.03 \text{ \AA}$ accompanying the earlier noted

reaction (Allen, et al., 1980), in which HNC apparently is not born with enough internal energy to isomerize to the energetically lower HCN.

Theoretical rotational constants and predicted microwave frequencies are reported in the Table. For HCOH also included are rotational constants and rotational transition energies deduced from structures obtained from extensively correlated wave functions (Goddard, et al., 1981). The latter configuration interaction (CI) predictions should be the more reliable, and further comparisons with experiment for formaldehyde (Yamaguchi and Schaefer, 1980) support this view. However, these results suggest that the correlation contribution to the observed frequency is reasonably predictable for molecules of this type. For this reason, we

consider a better prediction of the ($0_{0,0} \rightarrow 1_{0,1}$) transition of protonated formaldehyde to be ~ 62.9 GHz. It is to be emphasized, however, that even our best estimates of these rotational energy differences are uncertain to ~ 1 GHz.

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cis hydroxycarbene

$E = -113.81027$

trans hydroxycarbene

$E = -113.81931$

Protonated formaldehyde

$E = -114.19087$

Table. Rotational constants and predicted microwave frequencies in GHz for H_3CO^+ and HCOH .

		<u>SCF</u>	<u>CI</u>	<u>SCF</u>	<u>CI</u>
A	206.2	304.5	289.6	292.1	280.6
B	35.0	36.9	36.2	36.8	36.1
C	29.9	32.9	32.2	32.7	32.0
$\Delta E(0_{0,0} \rightarrow 1_{0,1})$	64.9	69.8	68.4	69.4	68.1