The molecular structure of HCO\(^+\) by the microwave substitution method\(^a\)

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Precise measurements of the frequencies of the \(J = 0\rightarrow 1\) transition of HCO\(^+\), H\(^1\)CO\(^+\), HC\(^4\)O\(^+\), DCO\(^+\), D\(^1\)CO\(^+\), and DC\(^4\)O\(^+\) have been used to determine a substitution \(r_s\) molecular structure for HCO\(^+\). The bond distances obtained are \(r_s\) (CO) = 1.107(1) Å and \(r_s\) (CH) = 1.0930(1) Å. This is the first such microwave \(r_s\) structure to be determined for any molecular ion. The determined bond distances and the transition frequencies can be compared to the results of previous high quality \textit{ab initio} calculations and excellent agreement is found. An initial attempt to characterize the Doppler shifts of the HCO\(^+\) frequency due to ion drift in a dc discharge and a measurement of the \(J = 1\rightarrow 2\) transition of DCO\(^+\), and thus its centrifugal distortion constant, are also reported here.

INTRODUCTION

Microwave spectroscopy has been the most powerful method for determining precise molecular structures of small gas phase molecules since its initial development in the late 1940's. The most satisfactory microwave structure is the equilibrium type \(r_e\), but since it requires vibrational satellite data for each normal mode, this kind of structure has been obtained for only a few polyatomic molecules. The best alternative is the so-called substitution \(r_s\) structure,\(^1\)-\(^3\) normally within 0.004 Å or less of the \(r_e\) type in the bond distances, and these have been obtained for a great many molecules with up to about ten atoms. Here, only ground vibrational state data are required, and the nonrigidity effects are approximately accounted for by using shifts in moments of inertia when a given atom is isotopically substituted to find the center of mass coordinates of that atom. In this paper we report the first determination of such a microwave \(r_s\) structure for a molecular ion, HCO\(^+\).

The rotational spectrum of this species was first observed by radio astronomy in 1970 by Buhl and Snyder,\(^4\) who coined the term X-ogen for the unknown molecule responsible; it was identified as that of the ion HCO\(^+\) shortly afterward by Kempler.\(^5\) This assignment was not totally confirmed until 5 years later, when Snyder et al.\(^,6\)-\(^8\) observed the H\(^12\)CO\(^+\) transition in the interstellar medium, and we reported detection of the original X-ogen line in a laboratory hydrogen–carbon monoxide discharge.\(^8\) The controversy surrounding the identification of the X-ogen spectrum stimulated two very elaborate \textit{ab initio} calculations of the molecular structure of HCO\(^+\) by Wahlgren et al.\(^9\) and by Kraemer and Diercksen.\(^10\)

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and also led to a great deal of further radio-astronomical work.\(^11\)-\(^14\) A preliminary account of our extension of the laboratory measurements on HCO\(^+\) to a total of six isotopic species was presented in 1976 at the 31st Annual Symposium on Molecular Spectroscopy.\(^15\) Using our frequency for the DCO\(^+\) transition, Hollis et al.\(^16\) were able to detect it in the interstellar medium in 1976. They found very dramatic enhancement of the concentration of the deuterium species relative to the cosmic D/H ratio, and this finding has provided very strong support for the validity of ion–molecule reaction mechanisms that have been proposed for the formation of interstellar molecules.\(^17\)-\(^19\) They did not report a rest frequency for the DCO\(^+\) transition, but rather used our rest frequency to convert their Doppler profiles into velocity distributions. Two years later Guellin and Thaddeus\(^20\) used our laboratory frequency to locate and identify the spectrum of H\(^13\)O\(^+\) in the interstellar medium. The spectra of HCO\(^+\) and its isotopic variants have become very important in astronomy as probes of cloud structure, dynamics, etc. in recent years. Guellin et al.\(^21\) have detected the J = 1–2 transition of DCO\(^+\) in five sources, and the DCO\(^+\)/HCO\(^+\) ratio has been studied by Watson et al.\(^22\) The J = 2–3 lines of HCO\(^+\) were observed in Orion by Huggins et al.\(^23\) and further studied by Erickson et al.\(^24\) Langer et al.\(^25\) have made further observations of HCO\(^+\) isotope ratios in the interstellar medium, and Penzias\(^26\) has related some measurements of H\(^13\)O\(^+\)/DCO\(^+\) to the galactic deuterium gradient. Stark and Wolff\(^27\) have reported observation of HCO\(^+\) in an external galaxy, and several other papers have considered the abundance of HCO\(^+\) in relation to that of other molecules in various parts of the interstellar medium.\(^28\)-\(^33\) In our laboratory, an extensive study of pressure broadening of HCO\(^+\) is underway, and the initial results on broadening of HCO\(^+\) by hydrogen with liquid nitrogen cooling have been published.\(^34\) Also, Haese and Woods\(^35\) have reported a CI dipole moment (4.07 D) for HCO\(^+\) and several related molecules.

For the isoelectronic molecular ion N\(_2\)H\(^+\), a similar substitution structure has been obtained and will be reported in the following paper.\(^36\) At present the only other molecular ions for which microwave data have been definitely assigned are the diatomic CO\(^37\) and HCO\(^+\)'.

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sulfur analog, HCS, recently discovered in the interstellar medium by Thaddeus et al. and confirmed by laboratory work in this group. Hopefully, isotopic work will ultimately lead to a substitution structure of HCS too.

EXPERIMENTAL

The instrumentation and the general experimental conditions in this work were essentially the same as those employed in the initial laboratory detection of HCO. The frequency measurement scheme was also the same as used in that original work and described in earlier papers, i.e., the klystron was not phase locked, but its frequency sweep was referenced to markers. Scans to high frequency were paired with matched scans to low frequency to form so-called sets and many sets were obtained and averaged for each transition to reduce the random error. Although a more sophisticated phase locked, digitally programmed microwave source is now available, the additional precision in frequency measurement that it provides would not be expected to change the structural results determined here in any significant way. The observation of the \( J=1-2 \) transition of DCO was made by doubling the output of an OKI 70V11A klystron with a Baytron 1E-80/G doubler (1E-5H diode) and detecting with a Baytron 1G-5A wafer mount with a 1E-5/X diode.

The available signal to noise ratio makes impractical detection of even \(^{13}\)C in natural abundance. We used 99% \(^{13}\)CO and 99% \(^{13}\)CO in these experiments (along with pure D\(_2\) for the deuterium species) so the signal strengths were about the same for the isotopic variants as for the main form. Only 1 liter (STP) of each rare form of CO, however, was available, and with the flow rate employed, this limited the total running time for each to only 10–12 h and correspondingly restricted the number of frequency measurements (sets) that could be averaged.

DOPPLER SHIFTS

As was mentioned in our earlier letter on the microwave spectrum of HCO the measurement of the frequencies in the spectrum of an ion in a dc discharge is complicated by a Doppler shift due to the systematic component of ion velocity along the electric field (axial) direction. This drift velocity is of course the product of the ion mobility, which by naive kinetic theory arguments is inversely proportional to pressure, and the electric field strength, which is a constant, at least along the positive column portion of the discharge. Our initial attempt to characterize these Doppler shifts is summarized in Fig. 1, which is a plot of measured frequency of the main HCO line versus reciprocal pressure. The right side of the graph corresponds to data with the klystron at the anode end and the left to measurements made when the klystron was moved to the cathode end of the cell. A total of 58 measurement sets are included, and the straight line shown is the best as determined by linear least squares. The fit to the linear model is very poor, but there is a clearly significant difference between the two directions of propagation, and the general magnitude of the effect is revealed. The slope of the line is 0.43 MHz mTorr, corresponding to a drift velocity of 140 m/sec at 10 mTorr pressure, which is quite reasonable. The scattered observed signal is partly due to the lack of precision in the frequency measurements for single sets and partly due to the fact that velocity depends on more than just the pressure, e.g., the electric field, the gas composition, the current, or the temperature. Despite the obvious limitations of these data, we have used the pressure correction implied by the linear fit to correct the frequencies for the other isotopic forms, where such extensive work was out of the question, on the assumption that this crude correction was better than none at all. New studies of the Doppler shifts and the rest frequencies with greatly improved measurement precision and control of experimental conditions are in progress and will be reported later. The effect is a very important one, since it can provide important dynamical information about the ions in the discharge, and the mere observation of it provides unambiguous proof that the spectrum is that of a positive ion (or a negative ion).

FREQUENCIES AND STRUCTURES

The determined rest frequencies are given in Table I. The main isotope frequency comes directly from the intercept in Fig. 1, and those of all the other isotopic forms come from an average of four to ten sets of measurements. The latter have been corrected for the Doppler effect using the linear shift of the preceding section (scaled according to center frequency). The errors shown are merely statistical 95% confidence limits (Student t distribution) reflecting the scatter among the different sets. They should be increased to about \( \pm 50 \) kHz to allow for inadequacies in the Doppler corrections, and any other nonrandom errors. In the case of DCO we can calculate the constants \( B_0(36019.797 \pm 0.025 \text{ MHz}) \) and \( D_0(0.0587 \pm 0.0054 \text{ MHz}) \). For the structure calculations we employed effective rotational constants \( B_{\text{eff}} = B_0 - 2D_0 = \frac{1}{2} \nu_{0,1} \) for all isotopic varieties.
TABLE I. Rest frequencies (in MHz) for various isotopic forms of HCO*.

<table>
<thead>
<tr>
<th></th>
<th>This work</th>
<th>Radio astronomy</th>
<th>KID</th>
<th>KD</th>
<th>WLPS*</th>
</tr>
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<tbody>
<tr>
<td>J = 0−1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO*</td>
<td>89 188, 523(2)</td>
<td>89 188, 55(10)b</td>
<td>89 610</td>
<td>89 190</td>
<td>89 360</td>
</tr>
<tr>
<td>H^12CO*</td>
<td>86 754, 329(39)</td>
<td>86 754, 4(2)c</td>
<td>87 250</td>
<td>86 760</td>
<td></td>
</tr>
<tr>
<td>DCO*</td>
<td>72 039, 350(33)</td>
<td>72 390</td>
<td>71 980</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D^12CO*</td>
<td>70 733, 218(21)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DC^18O*</td>
<td>68 827, 397(10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| J = 1−2 |           |                 |     |    |       |
| DCO*    | 144 077, 310(104) |          |       |       |       |
| J = 2−3 |           |                 |     |    |       |
| HCO*    | 267 557, 20(46)c |          |       |       |       |

*Reference 10.
Reference 14.
Reference 28.
Reference 7.
Reference 23.

All J = 0−1 transition frequency errors should be increased to 0.05 MHz to account for possible systematic errors (see the text); those shown are statistical only.

Reference 9.

including DCO*. Ignoring centrifugal distortion in this way has a negligible impact in the computed structural parameters. Table I also includes results from radio astronomy where available, the ab initio results of Walshgren et al., and two sets of predictions from the work of Kraemer and Dierckson. One is their pure ab initio CI results, where they calculate r_s's (and thus B_r) and also an anharmonic force field and the vibration-rotation interaction constants (and thus B_0). The other is a corrected ab initio result, where the bond distances and the harmonic force constants were scaled in the same way as was required to obtain agreement between theory and experiment in the case of the reference molecule HCN. Table I indicates that their proce-

TABLE II. Structure of HCO* (in Å) compared to that of HCN.

<table>
<thead>
<tr>
<th></th>
<th>r_s (1)a</th>
<th>r_s (2)a</th>
<th>r_s (avg)</th>
<th>r_s** b</th>
<th>CI</th>
<th>CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO*</td>
<td>1.1072</td>
<td>1.0929</td>
<td>1.0931</td>
<td>1.0930(1)b</td>
<td>1.095</td>
<td>1.095</td>
</tr>
<tr>
<td>r(CO)</td>
<td></td>
<td>1.1069</td>
<td>1.1057</td>
<td>1.103</td>
<td>1.1045</td>
<td></td>
</tr>
<tr>
<td>r(CH)</td>
<td>0.00116</td>
<td>0.00153</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m_e r_i</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HCN

<table>
<thead>
<tr>
<th></th>
<th>r(CN)</th>
<th>r(CH)</th>
<th>m_e r_i</th>
<th>r_s (true)c</th>
<th>PSHb</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(CN)</td>
<td>1.1555*</td>
<td>1.0631*</td>
<td>-0.00316</td>
<td>-0.00411</td>
<td>PSN*</td>
</tr>
<tr>
<td>r(CH)</td>
<td>1.1550*</td>
<td>1.0632*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m_e r_i</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*Combination (1) included HCO*, DCO*, H^12CO*, and HC^18O*; combination (2) included DCO*, HCO*, D^12CO*, and DC^18O*. The analogous combinations are used for HCN.

Using ab initio α constants of Kraemer and Dierckson (Ref. 10) and B_0's from this work.

Reference 10.
Reference 9.
Reference 43.
Reference 45.
Reference 44.

The errors shown reflect the effects of frequency measurement accuracy and the sensitivity of the r_s structure to the choice of parent species, but in no way reflect the expected level of agreement between r_s and the true r_s. See the text.

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The procedure works very well indeed in this case.

From the available collection of isotopic data a substitution structure may be calculated in two ways: (1) with HCO as the parent species and single substitutions at each atom, and (2) with DCO as the parent species and all single substitutions. The \( r_s \) values from these two combinations, which are not totally independent, since both use HCO and DCO data, are given in the first and second columns of Table 11, respectively, while column three contains the average of the two, which we consider to be our final best result. The quantity \( \sum \rho_{m} c_{m} \), which is identically zero for the true center of mass coordinates of a rigid rotor, is also shown. Its small value offers a pleasing indication of consistency. All the corresponding results for HCN are also shown in Table II: these were calculated from the literature \( B_{at} \) values for the equivalent isotope combinations.\(^{41}\) Not only do the results in the first two columns agree very closely (0.0003 Å), but whatever differences occur are essentially the same for HCO as for HCN. Table II also contains the \( a \) CI structures (\( r_s \)) of Kraemer and Dierckson\(^{10}\) for HCO and HCN, and of Wahlgren et al.\(^{9}\) for HCO and Pearson et al.\(^{42}\) for HCN. The agreement is quite good for all calculations, but a detailed comparison should take into account the fact that the theory predicts \( r_s \) while the experiment measures \( r_a \). In order to pursue this point we have taken the \( ab \) initio vibration-rotation interaction constants (\( \alpha 's \)) of Kraemer and Dierckson\(^{10}\) and combined them with our experimental \( B_{ex} \) to obtain estimates for the \( B_{ex} \) 's (called \( B_{ex}' \)). These were then used to calculate the \( r_s \) values for HCO that are shown in Table II by employing the substitution type computation, i.e., principal axis coordinates are obtained from isotope shifts (in the \( B_{ex}' \) 's rather than the \( B_{ex} \) 's). The quantity \( r_s \) defined by Pearson et al.\(^{42}\) for the isoelaticronic HNC molecule is similar in that the same \( B_{ex}' \) (namely experimental \( B_{ex}' \) corrected with the smaller basis set, pure CI \( \alpha 's \) of Hennig et al.\(^{41}\)) are used, but differs in that the \( r_b \) type calculation is used to calculate \( r_s \) from \( B_{ex}' \), i.e., a single pair of isotopic forms is used to calculate the two bond distances and then the results are averaged over many possible choices of the isotopic pair. The limitations of this concept (\( \rho 's \)) have been discussed by Creswell and Roblette.\(^{41}\) For reference, the accepted true \( r_s \) structure of HCN\(^{32}\) is shown in the same column. It must be emphasized that the \( r_s \) 's given for HCO are only estimates and do not constitute a true experimental determination of an equilibrium structure of HCO. If one compares the \( ab \) initio \( r_s \) 's to our \( r_s \) one sees that those of Kraemer and Dierckson\(^{10}\) agree more closely in the CI distance and those of Wahlgren et al.\(^{9}\) agree somewhat better in the CO distance. Hopefully more calculations of the quality of these two will be made, since they could be highly useful in predicting the micro-wave spectra of other molecular ions and thus shortening the very time consuming initial frequency search required.

A true \( r_s \) structure of HCO* would be highly desirable, and in fact essential if the comparison between theory and experiment is to be further tested or improved. With this in mind we have devoted considerable effort to searches for vibrational satellite spectra in the two stretching modes, but so far we have not detected any. (The first excited state of the bending mode does not possess a \( J=0-1 \) transition, and no attempt to detect its \( J=1-2 \) transition has been made.) This negative result indicates that the degree of vibrational excitation is lower for HCO* than for most neutral species that have been studied in our discharge tubes. Efforts will certainly continue because of both the interest in the \( r_s \) structure and that in the dynamics of vibrational excitation and relaxation in glow discharges.

\(^{1}\) J. Kratchman, Am. J. Phys. 21, 17 (1953).
\(^{19}\) D. Watson, Rev. Mod. Phys. 48, 513 (1976).
532 (1980).