# The rotational constant $A_0$ and planarity of the hydrogen-bonded complex $H_2CO\cdots HCl$

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A fit of $\mu_a$, R-branch transitions of the nearly prolate asymmetric rotor $H_2CO\cdots HCl$ ($\kappa \approx -0.99$) demonstrated that even a relatively large $A_0$ rotational constant can be determined with useful accuracy from such a limited set of data, provided the frequencies are of sufficient accuracy. Thus the set of spectroscopic constants $A_0$, $B_0$, $C_0$, $\Delta_J$, $\Delta_{JK}$, $\delta_J$, $\chi_{aa}$, $(\chi_{bb} - \chi_{cc})$, $\chi_{ab}$ and $\frac{1}{2}\{M_{bb} + M_{cc}\}$ are reported for $H_2CO\cdots H^{35}Cl$. The subsequent observation of two $\mu_b$, R-branch transitions led to a much more accurate value of $A_0$, but this did not lie outside the error of the preliminary value, confirming the usefulness of the initial approach. The inertial defect $\Delta_0 = 0.5724(1)$ u Å$^2$ demonstrates that the nuclei in $H_2CO\cdots H^{35}Cl$ are copolanar. Fits of limited numbers of $\mu_a$, R-branch transition frequencies for each of $H_2CO\cdots H^{37}Cl$, $D_2CO\cdots H^{35}Cl$ and $D_2CO\cdots H^{37}Cl$ led to $\Delta_0$ values for the isotopomers identical within experimental error to that of $H_2CO\cdots H^{35}Cl$.

## 1. Introduction

A group of complexes that have featured prominently in gas-phase investigations aimed at understanding the hydrogen bond are the $B\cdots HX$ complexes, where B is a simple Lewis base and X is a halogen atom. As a result of characterising a number of $B\cdots HX$ complexes through their rotational spectra, a set of rules for rationalising the angular geometries were put foward.[1,2] One of the rules requires simply that the electrophilic region $^{\delta+}H$ of HX seeks out the axis of a non-bonding electron pair (n-pair) carried by the acceptor atom of B, so that in the equilibrium geometry the HX axis coincides with the n-pair axis. Of particular significance in this respect are those complexes having an angular geometry of lower symmetry than the isolated molecule B, for then the direction of the hydrogen bond is evidently not determined by symmetry.

An example of such a complex is $H_2CO\cdots HCl$, for which a planar structure of $C_s$ symmetry is predicted by the rules. This complex was first investigated by Fraser *et al.*[3] who found an angle $\angle CO\cdots H \approx 110°$ but with a non-linear hydrogen bond (see Fig. 1). They established the geometry from the spectroscopic constants of the four isotopomers $H_2CO\cdots H^{35}Cl$, $H_2CO\cdots H^{37}Cl$, $D_2CO\cdots H^{35}Cl$ and $D_2CO\cdots H^{37}Cl$ under the reasonable assumption of coplanar nuclei based on the analogy with $H_2CO\cdots HF$.[4] They were not able to determine the rotational constant $A_0$ and therefore could not obtain the inertial defect $\Delta_0 = I_c^0 - I_b^0 - I_a^0$, which is a useful criterion of planarity.

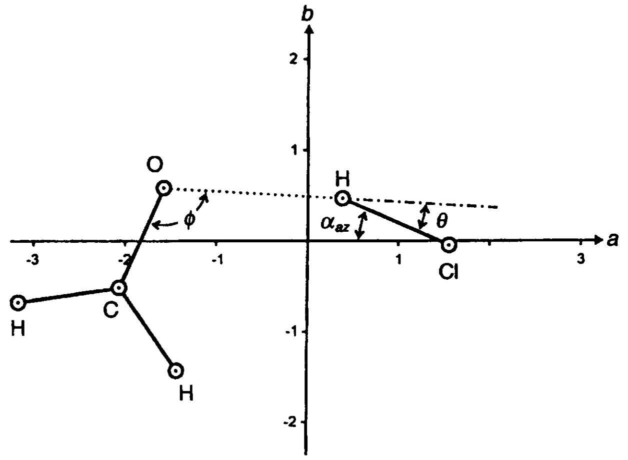

**Fig. 1** Geometry of $H_2CO\cdots H^{35}Cl$ determined as described in the text. The diagram is to scale and the axes are marked in units of 1 Å. The angles $\phi$, $\theta$ and $\alpha_{az}$ used in the text to discuss the angular geometry are defined.

In most spectroscopic investigations of weakly bound complexes, as with that of $H_2CO\cdots HCl$,[3] to generate a number of complexes sufficient for detection by rotational spectroscopy a supersonic expansion of the two components, highly diluted in argon, is used. However, the required very low effective temperature so achieved also has disadvantages. In general, when the complex $B\cdots HX$ is an asymmetric rotor, the relatively long, weak hydrogen bond ensures that the rotor lies close to the prolate limit (*e.g.* Ray's $\kappa = -0.99$ for $H_2CO\cdots H^{35}Cl$).[3] Moreover, when B is a small molecule, like $H_2CO$, the rotational constant $A_0$ is large and often $\mu_a$ is either the only or the predominant component of the electric dipole moment. Then, only $\mu_a$, R-branch transitions of low $J$ value are likely to be detected in the ground-state rotational spectrum because higher $J$ levels are effectively depopulated in the supersonic expansion and $\mu_b$ transitions either have zero or low intensity, or lie outside the range of the spectrometer. It is well known that $\mu_a$ transitions of nearly prolate, asymmetric rotors have a weak dependence on $A_0$. This is the reason that $A_0$ was not determined for $H_2CO\cdots HCl$ in ref. 3. Instead, it was held at the value implied by the final geometry when the rotational constants $B_0$ and $C_0$, the centrifugal distortion constants $\Delta_J$ and $\Delta_{JK}$, and the Cl-nuclear quadrupole coupling constants $\chi_{aa}(Cl)$ and $\chi_{bb}(Cl) - \chi_{cc}(Cl)$ were evaluated by fitting the $\mu_a$, R-branch transitions.

In this article, it will be established, by reference to the example of $H_2CO\cdots HCl$, that $A_0$ can in fact be estimated with useful accuracy by fitting only $\mu_a$, R-branch transitions of a nearly prolate, asymmetric-rotor complex when the frequencies are measured with good accuracy, as they were in ref. 3. To demonstrate that the standard error of $A_0$ so generated is a realistic indicator of precision, $\mu_b$-transitions for the isotopomer $H_2CO\cdots H^{35}Cl$ have been identified and used to obtain a very accurate $A_0$ value. As a result, the inertial defect of $H_2CO\cdots HCl$ has been determined and the planarity of the complex established.

## 2. Experimental

Ground-state rotational transitions of $H_2CO\cdots H^{35}Cl$ were observed by using a pulsed-nozzle, Fourier-transform microwave spectrometer.[5] A heated nozzle of the type described elsewhere[6] was used to generate formaldehyde *in situ* from paraformaldehyde (BDH). The circular channel concentric with the 0.7 mm hole in the base plate of the heated solenoid valve (General Valve Corp.) held the solid paraformaldehyde. When pulses of a gas mixture composed of 1% HCl (Argo International) in argon were expanded through the solenoid valve from a stagnation pressure of 3 bar, sufficient $H_2CO$ vapour above the warmed solid (temperature *ca.* 35 °C) was entrained in the gas to allow $H_2CO\cdots HCl$ complexes to be formed in the ensuing supersonic expansion.

Rotational transitions were recorded in the usual way and their frequencies were measured with an estimated accuracy of 2 kHz.

**Table 1** Observed ground-state transition frequencies[a] for $H_2CO\cdots H^{35}Cl$

| transition $J'_{K_{-1}K_1} \leftarrow J''_{K_{-1}K_1}$ | $F' \leftarrow F''$ | $\nu_{obs}$/MHz |
|---|---|---|
| $2_{12} \leftarrow 1_{11}$ | $1/2 \leftarrow 1/2$ | 10280.9885 |
| | $3/2 \leftarrow 1/2$ | 10274.1588 |
| | $5/2 \leftarrow 5/2$ | 10266.4574 |
| $2_{02} \leftarrow 1_{01}$ | $5/2 \leftarrow 5/2$ | 10420.2178 |
| $2_{11} \leftarrow 1_{10}$ | $3/2 \leftarrow 1/2$ | 10598.4109 |
| | $1/2 \leftarrow 1/2$ | 10601.9410 |
| | $5/2 \leftarrow 5/2$ | 10590.4239 |
| $5_{15} \leftarrow 6_{06}$ | $13/2 \leftarrow 15/2$ | 9397.8480 |
| | $11/2 \leftarrow 13/2$ | 9397.2965 |
| | $9/2 \leftarrow 11/2$ | 9397.9260 |
| | $7/2 \leftarrow 9/2$ | 9398.4876 |
| $4_{14} \leftarrow 5_{05}$ | $11/2 \leftarrow 13/2$ | 14993.1261 |
| | $9/2 \leftarrow 11/2$ | 14993.0768 |

[a] Measured in the present work.

## 3. Results

The geometry of $H_2CO\cdots HCl$ determined in ref. 3 implies non-zero values of the components $\mu_a$ and $\mu_b$ of the electric moment. Hence, *b*-type transitions are in principle observable. However, $\mu_b$ is likely to be smaller than $\mu_a$ because the projections of the component dipole moments $\mu_{H_2CO} = 2.332$ D,[7]† and $\mu_{HCl} = 1.1085(5)$ D[8] onto the *b*-axis are of opposite sign and therefore partially self-cancelling (see Fig. 1). Moreover, a prediction using the experimental $B_0$ and $C_0$ with $A_0$ calculated from the published geometry[3] shows that only the $4_{14} \leftarrow 5_{05}$ and $5_{15} \leftarrow 6_{06}$ transitions fall within the range of our spectrometer. The relatively high *J* value of these transitions coupled with the smaller $\mu_b$ value suggests they will not be as strong as the lower *J*, $\mu_a$ R-branch transitions in a jet expansion. To search for them at high sensitivity, it is therefore preferable to have a reasonable initial value of $A_0$, since an error of, say, 1 GHz in $A_0$ when predicted from the geometry implies a range of 1 GHz in the predicted frequency of these transitions. Consequently, the following approach to $A_0$ was used.

The frequencies of some additional Cl-nuclear quadrupole hyperfine components of the six $\mu_a$, R-branch transitions reported in ref. 3 were measured first. These are given in Table 1. The full set of $\mu_a$, R-branch transition frequencies (from ref. 3 and Table 1) were then fitted in an iterative least-squares analysis in which the Hamiltonian of eqn. (1) was constructed in $\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{J}$ basis and diagonalized.

$$H = H_R + H_Q + H_{SR} \tag{1}$$

In eqn. (1), $H_R$ is the semirigid rotor energy operator in the Watson A reduction[9] while $H_Q$ and $H_{SR}$ are the familiar Cl-nuclear quadrupole and spin–rotation coupling operators. If $H_2CO\cdots HCl$ is planar, the only non-zero components of the conventionally defined Cl nuclear quadrupole coupling tensor $\chi_{\alpha\beta} = -(eQ/h)\partial^2 V/\partial\alpha\,\partial\beta$ are $\chi_{aa}$, $\chi_{bb}$, $\chi_{cc}$ and $\chi_{ab}$. In principle, the diagonal components $M_{aa}$, $M_{bb} - M_{cc}$ and Tr($\boldsymbol{M}$) of the spin–rotation coupling tensor $\boldsymbol{M}$, are determinable.

In fitting the full set of $\mu_a$, R-branch transitions, it was found that only the spectroscopic constants $A_0$, $B_0$, $C_0$, $\Delta_J$, $\Delta_{JK}$, $\delta_J$, $\chi_{aa}$, $\chi_{bb} - \chi_{cc}$, $\chi_{ab}$ and $\frac{1}{2}(M_{bb} + M_{cc})$ made a significant contribution to the frequencies and the remaining constants were set to zero. The values from the final cycle of the fit are given in column I of Table 2, together with the standard deviation $\sigma$ of the fit. We note that $\sigma$ is comparable with the estimated accuracy of frequency measurement. The most interesting features of the constants in column I of Table 2 are the relatively small standard errors associated with $A_0$ and $\chi_{ab}$, both of which constants are not normally expected to be determined in fits of $\mu_a$, R-branch transitions of a nearly prolate asymmetric rotor. In fact, even when the additional Cl-nuclear quadrupole hyperfine frequencies measured here (Table 1) are removed from the fit, the determined values of $A_0 = 44437(148)$ MHz and $\chi_{ab} = 28(4)$ MHz are almost as

**Table 2** Spectroscopic constants[a] for four isotopomers of $H_2CO\cdots HCl$

| | $H_2CO\cdots H^{35}Cl$ | | | | |
|---|---|---|---|---|---|
| spectroscopic constant | I[b] | II[c] | $H_2CO\cdots H^{37}Cl$[d] | $D_2CO\cdots H^{35}Cl$[d] | $D_2CO\cdots H^{37}Cl$[d] |
| $A_0$/MHz | 44441 (116) | 44454.181 (7) | 44290 (179) | 36463 (147) | 36498 (135) |
| $B_0$/MHz | 2687.8795 (9) | 2687.8810 (5) | 2622.922 (2) | 2550.236 (2) | 2487.102 (3) |
| $C_0$/MHz | 2527.3727 (8) | 2527.3717 (8) | 2469.793 (2) | 2377.817 (2) | 2322.771 (3) |
| $\Delta_J$/kHz | 11.03 (3) | 11.05 (2) | 10.54 (6) | 9.81 (9) | 9.40 (9) |
| $\Delta_{JK}$/kHz | −236.4 (6) | −236.6 (2) | −233.4 (9) | −131.3 (13) | −130.6 (11) |
| $\delta_J$/kHz | 0.97 (2) | 1.01 (2) | 0.89 (5) | 0.86 (6) | 0.80 (9) |
| $\chi_{aa}$/MHz | −41.425 (3) | −41.426 (3) | −32.682 (5) | −39.851 (7) | −31.440 (10) |
| $(\chi_{bb} - \chi_{cc})$/MHz | −13.199 (7) | −13.192 (7) | −10.36 (2) | −14.69 (2) | −11.53 (2) |
| $\chi_{ab}$/MHz | 29.5 (28) | 31.0 (27) | 18 (7) | 33.5 (29) | 24 (8) |
| $\frac{1}{2}(M_{bb} + M_{cc})$/kHz | −0.73 (26) | −0.74 (27) | −0.6 (4) | — | — |
| $\Delta_0$/u Å$^2$ | 0.57 (3) | 0.5724 (1) | 0.54 (5) | 0.51 (5) | 0.53 (5) |
| $\chi_{ab}^{calc}$/MHz | 30.1 | 30.1 | 23.7 | 31.4 | 24.7 |
| $\sigma$/kHz[e] | 3.0 | 3.0 | 3.0 | 5.4 | 5.8 |

[a] The A-reduction of Watson and the $I^r$ representation were used. [b] Obtained by fits of measured frequencies of $\mu_a$ transitions from ref. 3 and Table 1. [c] $\mu_b$ transitions from Table 1 are also included in fit. [d] Only $\mu_a$ transition frequencies from ref. 3 were fitted. [e] Standard deviation of fit.

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† 1 D (Debye) ≈ 3.335 64 × $10^{-30}$ C m.

precise as those obtained from the fit of the full set of $\mu_a$, R-branch data. Hence, the extra components reported here are not essential for the determination of $A_0$ but slightly improve it.

Encouraged by the relatively small error in $A_0$, a search was made for the *b*-type transitions $4_{14} \leftarrow 5_{05}$ and $5_{15} \leftarrow 6_{06}$. Although quite weak, they were found within a few MHz of their predicted frequencies and were positively identified by their characteristic nuclear quadrupole hyperfine structure. Observed frequencies are included in Table 1.

When the *b*-type transitions were added to the least-squares fit, the set of spectroscopic constants given in column II of Table 2 was obtained. The value of $A_0$ now has a very small error. Also included in Table 2 is the inertia defect $\Delta_0 = I_c^0 - I_b^0 - I_a^0$. Klemperer and co-workers[4] showed by careful analysis of the Stark effect in $H_2CO\cdots HF$ that the component $\mu_c$ of the electric dipole moment is negligibly small and that therefore the nuclei are copolar. The result $\Delta_0 = 0.5724(1)$ u Å$^2$ for $H_2CO\cdots H^{35}Cl$ from column II of Table 2 is very similar to that ($\Delta_0 = 0.62$ u Å$^2$) determined for $H_2CO\cdots HF$,[4] and this establishes that $H_2CO\cdots HCl$ is also a planar complex, as assumed in its original investigation.[3]

Another feature of the sets of spectroscopic constants in columns I and II of Table 2 is the fact that the off-diagonal element $\chi_{ab}$ of the Cl-nuclear quadrupole coupling tensor $\chi_{\alpha\beta}$ is determined, albeit with an error of 2.7 MHz. Is $\chi_{ab}$ merely a fitting parameter of no physical significance or is it realistic? This question can be answered as follows. In a weakly bound complex $B\cdots HCl$, it is reasonable to assume that the cylindrical symmetry of the electric charge distribution of HCl is not greatly perturbed by complex formation. If the cylindrical symmetry of the HCl molecule were not perturbed by complex formation, so that $\chi_{xx} = \chi_{cc} = -\frac{1}{2}\chi_{zz}$, where $x$ is in the plane but perpendicular to the HCl bond and $z$ is along the HCl bond, it is readily shown that the off-diagonal element is given by

$$\chi_{ab}^2 = \chi_{aa}\chi_{bb} + 2\chi_{cc}^2 \qquad (2)$$

When $\chi_{aa}$, and $\chi_{bb} - \chi_{cc}$ from Table 2 are used in eqn. (2), the resulting value $\chi_{ab}^{\text{calc}} = 30.1$ MHz is the same within experimental error as that obtained from the least-squares fit, illustrating that the fitted quantity is indeed physically realistic (see Table 2).

Although no further transitions of the isotopomers $H_2CO\cdots H^{37}Cl$, $D_2CO\cdots H^{35}Cl$ and $D_2CO\cdots H^{37}Cl$ have been measured, the fact that $A_0$ can be determined with reasonable accuracy from $\mu_a$, R-branch transitions alone (compare columns I and II of Table 2 for the case $H_2CO\cdots H^{35}Cl$) suggests that the frequencies for these isotopomers from ref. 3 are sufficient to allow $A_0$ values to be established. The resulting sets of spectroscopic constants are given in Table 2. Again the $\sigma$ values show that the fits are satisfactory, given the additional uncertainties arising from the D-nuclear quadrupole structure in the $D_2CO$ species.[3] The errors in the $A_0$ values are relatively small and the inertial defects $\Delta_0$ are isotopically invariant within experimental error. The values $\chi_{ab}^{\text{calc}}$ obtained from eqn. (2) are also given in Table 2. It is of interest to note that the observed $\chi_{ab}$ values are in agreement with $\chi_{ab}^{\text{calc}}$ within experimental error in all cases, although admittedly the error is quite large for the $^{37}$Cl-based isotopomers.

## 4. Discussion

It has been shown by using the example of $H_2CO\cdots H^{35}Cl$ that a fit of only $\mu_a$, R-branch transitions for a nearly prolate asymmetric rotor ($\kappa = -0.9923$) can lead to a usefully accurate value of $A_0$. Moreover, it is also possible to determine the complete Cl-nuclear quadrupole coupling tensor. Although the observed frequencies have only a weak dependence of $A_0$ and $\chi_{ab}$, the high accuracy with which the frequencies can be measured by means of pulsed-nozzle, FT microwave spectroscopy provides the key to their determination.

By using the initial value of $A_0$ so established, two *b*-type transitions were found for $H_2CO\cdots H^{35}Cl$ and measured. When these were included in the fit, it was found that the accurate value of $A_0$ obtained agreed with the initial value to well within the experimental error of the latter. The accurate value of $\Delta_0$ establishes the planarity of the complex.

Frequencies of $\mu_a$, R-branch transitions for the isotopomers $H_2CO\cdots H^{37}Cl$, $D_2CO\cdots H^{35}Cl$ and $D_2CO\cdots H^{37}Cl$ already in the literature were fitted and gave $A_0$ values of acceptable accuracy. The resulting $\Delta_0$ values showed that this quantity is isotopically invariant. For all isotopomers, $\chi_{ab}$ obtained from the fit agreed within experimental error with $\chi_{ab}^{\text{calc}}$ calculated from eqn. (2).

The geometry reported for $H_2CO\cdots HCl$ in ref. 3 predicted $A \approx 42$ GHz for $H_2CO\cdots H^{35}Cl$ and $H_2CO\cdots H^{37}Cl$ and $A \approx 35$ GHz for $D_2CO\cdots H^{35}Cl$ and $D_2CO\cdots H^{37}Cl$. Given the usual uncertainties introduced by zero-point effects, these values are in excellent agreement with those determined here. When the principal moments of inertia $I_a^0$, $I_b^0$ and $I_c^0$ of $H_2CO\cdots H^{35}Cl$ and $H_2CO\cdots H^{37}Cl$ were fitted to obtain the distance $r(O\cdots H)$ and the angle $\phi$ (see Fig. 1) under the constraint that the angle $\alpha_{az}$ (Fig. 1) between the HCl axis $z$ and the *a*-axis in the equilibrium conformation of $H_2CO\cdots H^{35}Cl$ takes the value 23.66° implied by

$$\alpha_{az} = \tfrac{1}{2}\tan^{-1}[-2\chi_{ab}/(\chi_{aa} - \chi_{bb})] \qquad (3)$$

it is found that $r(O\cdots H) = 1.968(10)$ Å, $\phi = 110.0(10)°$ and that the non-linearity of the hydrogen bond $\theta = 20.3°$ (see Fig. 1). The geometries of the monomers $H_2CO$[10] and HCl† were assumed unchanged on formation of the complex. The details of the least-squares fitting procedures and the deviation of eqn. (3) are set out in ref. 12. When the corresponding approach is applied to $D_2CO\cdots H^{35}Cl$ and $D_2CO\cdots H^{37}Cl$ the results are $\alpha_{az} = 25.07°$, $r(O\cdots H) = 1.960(10)$ Å, $\phi = 109.6(8)°$ and $\theta = 20.5°$. Thus, the determined geometry of the complex is effectively independent of the deuteriation of $H_2CO$. It should be mentioned that the approach set out in ref. 12 is entirely equivalent to that used in the initial work on $H_2CO\cdots HCl$[3] and first introduced by Klemperer and co-workers for $H_2CO\cdots HF$.[4] The geometry presented here for $H_2CO\cdots HCl$ is not signicantly different from that reported in ref. 3.

## References

1 A. C. Legon and D. J. Millen, *Faraday Discuss. Chem. Soc.*, 1982, **73**, 71.
2 A. C. Legon and D. J. Millen, *Chem. Soc. Rev.*, 1987, **16**, 467.
3 G. T. Fraser, C. W. Gillies, J. Zozom, F. J. Lovas and R. D. Suenram, *J. Mol. Spectrosc.*, 1987, **126**, 200.
4 F. A. Baiocchi and W. Klemperer, *J. Chem. Phys.*, 1983, **78**, 3509.
5 A. C. Legon, in *Atomic and Molecular Beam Methods*, ed. G. Scoles, Oxford University Press, Oxford, 1992, ch. 9.
6 A. C. Legon and N. W. Howard, *J. Chem. Phys.*, 1987, **86**, 6722.
7 B. Fabricant, D. Krieger and J. S. Muenter, *J. Chem. Phys.*, 1977, **67**, 1576.
8 E. W. Kaiser, *J. Chem. Phys.*, 1970, **53**, 1686.
9 J. K. G. Watson, *J. Chem. Phys.*, 1968, **45**, 4517.
10 T. Oka, *J. Phys. Soc. Jpn.*, 1960, **15**, 2274.
11 F. C. DeLucia, P. Helminger and W. Gordy, *Phys. Rev. A*, 1971, **3**, 1971.
12 A. C. Legon, *Faraday Discuss. Chem. Soc.*, 1994, **97**, 19.

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† Calculated from $r_0 = [h/(8\pi^2\mu B_0)]^{1/2}$ using the $B_0$ value of $H^{35}Cl$.[11]