On the Ambiguity of Complex Structures Derived from one Set of Rotational Constants

H. Dreizler* and S. Kassi

Laboratoire de Physique des Lasers, Atomes et Molecules Université des Sciences et Technologies de Lille F-59655 Villeneuve d'Ascq

Z. Naturforsch. **53 a,** 743–746 (1998); received June 22, 1998

It is shown algebraically that from one set of rotational constants or moments of inertia of a complex formed by an asymmetric top molecule and a rare gas atom, eight generally different structures result which are compatible with the moments of inertia.

Introduction

In the last years many complexes containing a molecule and a rare gas atom like argon have been investigated [1, 2]. Especially molecular beam Fourier transform microwave (MB FTMW) spectroscopy has contributed a great deal to this field. Many publications showed that there exists an ambiguity in the determined structure [3]. In a number of cases this ambiguity could be reduced by using isotopomer complexes [4], ab initio calculations [3, 5], or arguments based on the nuclear quadrupole structure [5] or dipole moment [3]. In this paper we intend to show algebraically that for a complex of a rare gas atom attached to an asymmetric top molecule, eight generally different solutions result for the structure as determined from the one set of rotational constants or moments of inertia obtained from the spectrum.

Theoretical considerations

Part of the considerations follow those given for the r_s-structure [6, 7] explained in detail in [8]. We place a principal axis system (x, y, z; cm) in the center of mass (cm) of the asymmetric top base molecule and a second axis system (x', y', z'; CM) with the origin at the center of mass (CM) of the complex and with its axes parallel to the first system, as shown in Figure 1.

* Permanent address: Institut für Physikalische Chemie, Olshausenstr. 40, D-24098 Kiel

Reprint requests to Prof. H. Dreizler; Fax: +49 431 8801416, E-mail: dreizler@phc.uni-kiel.de.

In general, the (x', y', z'; CM) axis system is not a principal axis system of the complex. The position of a mass m_i is described by

$$\begin{aligned} \boldsymbol{r}_i &= \boldsymbol{r}_{\mathrm{CM}} + \boldsymbol{r}'_i \\ x_i &= x_{\mathrm{CM}} + x'_i \end{aligned} \quad \text{cyclic in } x, y, z. \tag{1 a-c}$$

For the atoms of the asymmetric top molecule we have, from the definition of the (x, y, z; cm) system,

$$\sum_i m_i \boldsymbol{r}_i = 0, \tag{2}$$

and for the molecular complex, from the definition of the (x', y', z'; CM) system,

$$\sum_i m_i \boldsymbol{r}'_i + M \boldsymbol{r}'_{\mathrm{M}} = 0, \tag{3}$$

where m_i is the mass of the ith atom in the molecule and M the mass of the rare gas atom. The moments of inertia of the base molecule in the (x, y, z, cm) system are

$$I_{xx} = \sum_i m_i (y_i^2 + z_i^2) \quad \text{cyclic in } x, y, z. \tag{4 a-c}$$

The products of inertia are

$$I_{xy} = -\sum_i m_i x_i y_i = 0 \quad \text{cyclic in } x, y, z. \tag{5 a-c}$$

The moments and products of inertia of the molecule in the (x', y', z'; CM) system may be expressed using (1) and (2) as

0932–0784 / 98 / 0900–0743 $ 06.00 © Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

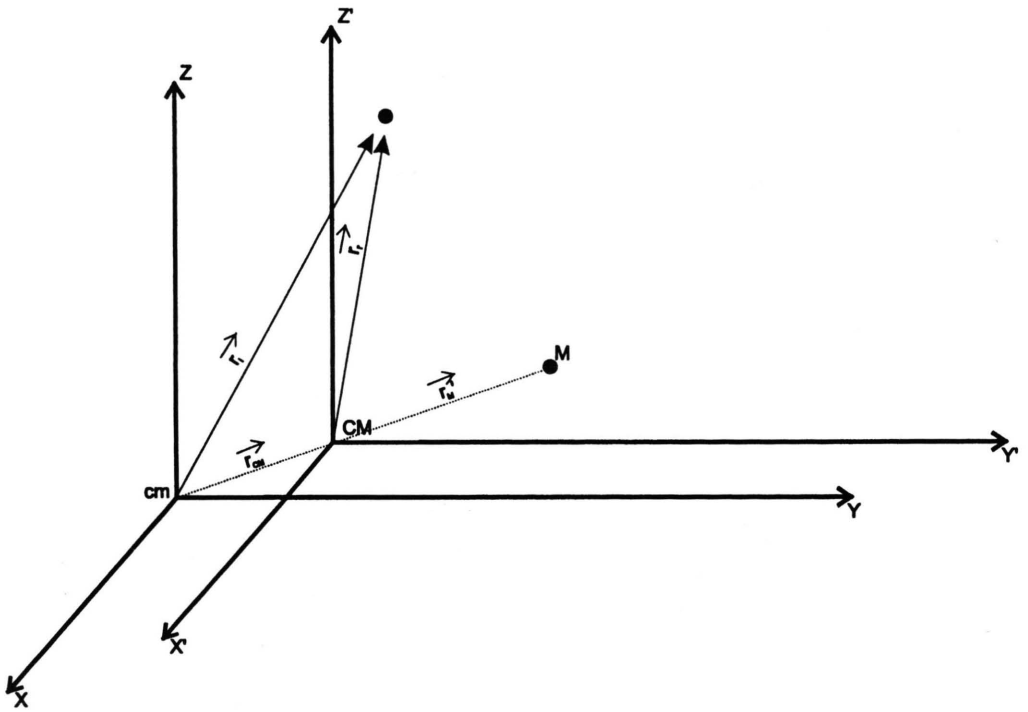

Fig. 1. Principal axis system (x, y, z; cm) of the asymmetric top base molecule and an axis system (x', y', z'; CM) originating in the center of mass (CM) of the complex. The axes x and x', y and y', z and z' are parallel. $\boldsymbol{r}_{\mathrm{M}} = \boldsymbol{r}_{\mathrm{CM}} + \boldsymbol{r}'_{\mathrm{M}}$ is colinear with $\boldsymbol{r}_{\mathrm{CM}}$ and $\boldsymbol{r}'_{\mathrm{M}}$.

$$\begin{aligned} I_{x'x'} &= \sum_i m_i(y_i'^2 + z_i'^2) \\ &= I_{xx} + m(y_{\mathrm{CM}}^2 + z_{\mathrm{CM}}^2) \end{aligned} \quad \text{cyclic in } x, y, z, \quad (6\text{ a-c})$$

and using (5)

$$\begin{aligned} I_{x'y'} &= -\sum_i m_i x_i' y_i' \\ &= -m x_{\mathrm{CM}} y_{\mathrm{CM}} \end{aligned} \quad \text{cyclic in } x, y, z. \quad (7\text{ a-c})$$

In (6) and (7) the total mass m of the molecule

$$m = \sum_i m_i \quad (8)$$

has been used. (6) and (7) give a formulation of Steiners law [9].

Next, the elements of the inertial tensor of the complex in the (x', y', z'; CM) system are given by

$$\begin{aligned} I^{(c)}_{x'x'} &= I_{x'x'} + M({y'_{\mathrm{M}}}^2 + {z'_{\mathrm{M}}}^2) \\ &= I_{xx} + m(y_{\mathrm{CM}}^2 + z_{\mathrm{CM}}^2) \quad \text{cyclic in } x, y, z, \quad (9\text{ a-c}) \\ &\quad + M({y'_{\mathrm{M}}}^2 + {z'_{\mathrm{M}}}^2) \end{aligned}$$

$$\begin{aligned} I^{(c)}_{x'y'} = I^{(c)}_{y'x'} &= I_{x'y'} - M x'_{\mathrm{M}} y'_{\mathrm{M}} \quad \text{cyclic in } x, y, z \\ &= -m x_{\mathrm{CM}} y_{\mathrm{CM}} - M x'_{\mathrm{M}} y'_{\mathrm{M}} \end{aligned} \quad (10\text{ a-c})$$

with the position of the rare gas atom in the (x', y', z'; CM) system

$$\boldsymbol{r}'_{\mathrm{M}} = (x'_{\mathrm{M}}, y'_{\mathrm{M}}, z'_{\mathrm{M}}). \quad (11)$$

The inertial tensor of the complex with the elements given in (6) and (7) is not necessarily expressed in its principal axis system. To calculate the principal moments of inertia of the complex, the secular equation

$$D = \begin{vmatrix} I^{(c)}_{x'x'} - \tilde{I} & I^{(c)}_{x'y'} & I^{(c)}_{x'z'} \\ I^{(c)}_{x'y'} & I^{(c)}_{y'y'} - \tilde{I} & I^{(c)}_{y'z'} \\ I^{(c)}_{x'z'} & I^{(c)}_{y'z'} & I^{(c)}_{z'z'} - \tilde{I} \end{vmatrix} = 0 \quad (12)$$

has to be solved.

The solutions of (12) for $\tilde{I}$ provide the three principal moments of inertia of the complex. We do not solve (12) explicitly but we prove that a position of the rare gas atom given by $x_{\mathrm{CM}}+x'_{\mathrm{M}}$, $y_{\mathrm{CM}}+y'_{\mathrm{M}}$, $z_{\mathrm{CM}}+z'_{\mathrm{M}} =$

x_M, y_M, z_M can be changed to $\pm x_M$, $\pm y_M$, $\pm z_M$ with an arbitrary choice of the signs. This results in eight different sign combinations, one for each octant of the (x, y, z; cm) system, without changing (12). Consequently the three $\tilde{I}$ are invariant under the mentioned choices of sign. In detail (12) may be rewritten as

$$\begin{aligned} D = &- \tilde{I}^3 + \tilde{I}^2(I^{(c)}_{x'x'} + I^{(c)}_{y'y'} + I^{(c)}_{zzx'}) \\ &- \tilde{I}^1(I^{(c)}_{x'x'}I^{(c)}_{y'y'} + I^{(c)}_{y'y'}I^{(c)}_{z'z'} + I^{(c)}_{z'z'}I^{(c)}_{x'x'} \\ &\quad - I^{(c)}_{x'y'}I^{(c)}_{y'x'} - I^{(c)}_{y'z'}I^{(c)}_{z'y'} - I^{(c)}_{z'x'}I^{(c)}_{x'z'}) \\ &+ \tilde{I}^0(I^{(c)}_{x'x'}I^{(c)}_{y'y'}I^{(c)}_{z'z'} + I^{(c)}_{x'y'}I^{(c)}_{y'z'}I^{(c)}_{z'x'} \\ &\quad + I^{(c)}_{x'z'}I^{(c)}_{z'y'}I^{(c)}_{y'x'} - I^{(c)}_{x'x'}I^{(c)}_{y'z'}I^{(c)}_{z'y'} \\ &\quad - I^{(c)}_{y'y'}I^{(c)}_{z'x'}I^{(c)}_{x'z'} - I^{(c)}_{z'z'}I^{(c)}_{x'y'}I^{(c)}_{y'x'}). \end{aligned} \tag{13}$$

Before considering (13), it may be stated that the center of mass of the complex CM is always between cm and M as shown in Fig. 1, which means that a change of sign from

$$\begin{aligned} x_M &= x_{CM} + x'_M \quad \text{to} \\ -x_M &= -x_{CM} - x'_M \quad \text{cyclic in } x, y, z. \end{aligned} \tag{14 a-c}$$

always induces a simultaneous change of sign of x_{CM} and x'_M

$$\begin{aligned} &\text{sign } x_M = \text{sign } x_{CM} = \text{sign } x'_M \\ &\text{cyclic in } x, y, z. \end{aligned} \tag{15 a-c}$$

It is immediatly obvious from (9) that all terms $I^{(c)}_{gg}$, $g = x', y', z'$, are invariant under the described changes of sign. The remaining terms like $I^{(c)}_{x'y'}I^{(c)}_{y'x'}$ and $I^{(c)}_{x'y'}I^{(c)}_{y'z'}I^{(c)}_{z'x'}$ are considered separately. According to (10) we have

$$I^{(c)}_{x'y'}I^{(c)}_{y'x'} = (m x_{CM} y_{CM} + M x'_M y'_M)^2. \tag{16}$$

Under the change of sign given in (14), the typical term $I^{(c)}_{x'y'}I^{(c)}_{y'x'}$ is invariant. With (10) the triple products are

$$\begin{aligned} I^{(c)}_{x'y'}I^{(c)}_{y'z'}I^{(c)}_{z'x'} = &-(m x_{CM} y_{CM} + M x'_M y'_M) \\ &\cdot (m y_{CM} z_{CM} + M y'_M z'_M) \\ &\cdot (m z_{CM} x_{CM} + M z'_M x'_M), \end{aligned} \tag{17}$$

where the coordinates x, y, z always occur pairwise within two of the three brackets,

$$\begin{aligned} \text{sign } I^{(c)}_{x'y'}I^{(c)}_{y'z'}I^{(c)}_{z'x'} = &-(\text{sign } x_{CM} \text{sign } y_{CM}) \\ &\cdot (\text{sign } y_{CM} \text{sign } z_{CM}) \\ &\cdot (\text{sign } z_{CM} \text{sign } x_{CM}). \end{aligned} \tag{18}$$

Equation (18) is obviously invariant with respect to a change of sign of x_{CM}, y_{CM}, and/or z_{CM}. The remaining terms behave in the same way. Then (12) and (13) are invariant with respect to the choice of any one of the eight possible positions of the rare gas atom M. Each of them yields the same set of moments of inertia, which represents the only experimental information available.

That means that from one set of rotational constants of the complex (plus the set of rotational constants of the base molecule alone) the position of the rare gas atom in the complex cannot be uniquely determined.

When the base molecule itself has certain symmetries, some of the eight possibilities are essentially equivalent. For example, it does not matter whether the rare gas atom is attached behind or before a symmetry plane of the base molecule. If the rare gas atom is attached on a principal plane of the molecule, the ambiguity reduces to four possibilities, since one coordinate vanishes, $g_M = 0$, $g = x$, y, or z. The furane-argon complex is an example [10 - 12]. For an attachment on a principal axis of the molecule, two possibilities remain.

In many cases [10], a complex has been considered to be the result of the substitution of a mass of zero attached to the base molecule (the "parent" molecule) by the mass M of the rare gas atom (resulting in the "isotopomer"). The r_s-method applied to this scheme also yields eight possible positions of the "substituted" atom, since only the magnitudes $|x_M|$, $|y_M|$, $|z_M|$ are determinable. However, this does not obviate the proof presented in this paper because the r_0-method used here (determination of the structure from inertial moments) and the r_s-method (essentially the determination of the structure from differences of inertial moments) are not strictly equivalent.

The ambiguity encountered is correlated with the D_{2h} symmetry of the inertial ellipsoid with three different axes. The D_{2h} group consists of eight operations. The deeper reason of the discussed ambiguity is the fact that the replacement of the molecular mass point system by its inertial ellipsoid reduces the available information.

Conclusion

Whenever we determine the structure of a complex made of a molecule and a rare gas atom, we should carefully check if all structural models have been considered that are compatible with the determined principal moments of inertia of the complex. The ambiguity could possibly be reduced by using additional features of the spectrum.

The consideration may be extended also to bimolecular complexes. Additional coordinates have to be considered here.

Acknowledgements

H. D. thanks the Lille group for hospitality and stimulating discussions and is grateful to the Région Nord Pas de Calais (France) for appointement as Visiting Research Professor in 1998. The Laboratoire de Spectroscopie Hertzienne is a "Unité de Recherche Associée au CNRS". The Centre d'Etudes et Recherches Lasers et Applications is supported by the Ministère Chargé de la Recherche, by the Région Nord-Pas de Calais, and by the Fonds de Développement Economique des Régions. The authors thank Prof. Dr. H. D. Rudolph, Ulm, and Prof. Dr. D. H. Sutter, Kiel, for critically reading the manuscript.

[1] K. R. Leopold, G. T. Fraser, S. E. Novick, and W. Klemperer, Chem. Rev. **94**, 1807 (1994).
[2] S. Sun and E. R. Bernstein, J. Phys. Chem. **100**, 13348 (1996).
[3] p. e. U. Spoerel, H. Dreizler, W. Stahl, E. Kraka, and D. Cremer, J. Phys. Chem. **100**, 14298 (1996).
[4] p. e. U. Kretschmer, W. Stahl, and H. Dreizler, Z. Naturforsch. **48a**, 1219 (1993).
[5] E. Kraka, D. Cremer, U. Spoerel, I. Merke, W. Stahl, and H. Dreizler, J. Phys. Chem. **99**, 12466 (1995).
[6] J. Kraitchman, Amer. J. Phys. **21**, 17 (1953).
[7] C. C. Costain, J. Chem. Phys. **24**, 864 (1958).
[8] W. Gordy and R. H. Cook, Microwave Molecular Spectra, John Wiley, New York 1984, Chapt. XIII.3.
[9] H. Goldstein, Classical Mechanics, Addison-Wesley, Cambridge, Mass., Chapt 5.3.
[10] S. G. Kukolich, J. Amer. Chem. Soc. **105**, 2207 (1983).
[11] S. G. Kukolich, J. Chem. Phys **77**, 5242 (1982).
[12] J. J. Oh, W. Hillig, R. H. Kuczkowski, and R. K. Bohn, J. Phys. Chem. **94**, 4453 (1990).