Chapter 13

Interstellar Molecules

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13.1   Introduction

Over a hundred molecules have recently been detected in the interstellar space. The largest of these corresponds to a linear system comprising 13 atoms: $HC_{11}N$. The detection of molecules in outer space is performed through radiotelescopes operating on the microwave and far-infrared electromagnetic regions. Because the signal features rarely hint at well-defined molecular origins, identification of such species becomes in most cases a far from trivial task.

In the course of proposing possible candidates to identify interstellar molecules, experience plays a fundamental role, which involves narrowing down the list of these

throughout a process of calculations and experiments employed to pinpoint the origin of the signal.

For example, in order to explain the notorious X-line, whose signal originates from five known sources: Orion, W3(OH), L134, SgrA and W51, several molecules were proposed as candidates. According to quantum chemical calculations and one experiment, this line was determined to be associated with the rotational transition between the ground and first excited state of HCO^+. The calculations further predicted the presence of transition frequencies, yet to be observed, arising from three isotopes of this species.

A more recent example corresponds to the discovery of the first magnesium-containing molecule in circumstellar atmosphere: MgNC. Although the experiment has apparently provided a definite answer in this regard, calculations performed up to date yield frequencies that remain relatively far from the observed one. This molecule represents a challenging example where, in order to theoretically obtain an acceptable figure for the rotational constant−in comparison to that inferred from the observed transition−refinements and improvements on ab initio methods in computational quantum chemistry are called for.

Beyond reproducing exact figures in accordance with obervations and experimental data, quantum chemical calculations serve the purpose of improving and testing the employed methods and techniques, thus delivering tools of theoretical analysis that can be used on more complex systems.

13.2 Molecular Rotation

According to the Born-Oppenheimer approximation [1] the molecular wave function can be written as

$$\psi(q, Q) \simeq \Phi(q; Q)\chi(Q) \ ,$$

where $\Phi(q; Q)$ corresponds to the electronic wave function that parametrically depends on the nuclear coordinate Q, while $\chi(Q)$ describes the nuclear motion, representing a solution of the Schrödinger equation for the nuclei:

$$\left\{ -\frac{\hbar^2}{2\mu} \bigtriangledown^2 + \epsilon(Q) \right\} \chi(Q) = E\chi(Q), \tag{13.1}$$

where $\epsilon(Q)$ denotes the electronic potential that is found by systematically solving the electronic problem for different nuclear configurations, and μ is the reduced nuclear mass. In general, Q denotes a set of collective coordinates of nuclei, which, for a diatomic molecule, corresponds to the internuclear distance, $Q = \vec{R}$. One can thus write

$$\chi(Q) = \chi(\vec{R}) = R(r)\Theta(\theta, \varphi),$$

which holds under the assumption that $\epsilon(Q) = \epsilon(r)$, i.e. when dealing with a central potential that only depends on the magnitude $r = |\vec{R}|$. The nuclear motion thus consists of a radial and an angular component. The latter fulfills Legendre's equation:

$$-\frac{\hbar^2}{2\mu R}\left(\frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\,\theta\frac{\partial}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\rho^2}\right)\Theta_{JM}(\theta, \varphi) = \frac{J(J+1)\hbar^2}{2\mu R^2}\Theta_{JM}(\theta, \varphi),$$

which can be recast as an eigenvalue equation for the total angular momentum,

$$\hat{J}^2\Theta_{JM} = J(J+1)\hbar^2\Theta_{JM}. \tag{13.2}$$

On the other hand, the magnitude of the angular momentum, $|\vec{J}|$, associated with a molecule rotating about the center of mass with angular frequency ω, is given by

$$|\vec{J}| = I\omega,$$

where I denotes the moment of inertia $I = \mu R^2$. It is convenient to write the rotational energy as

$$E = \frac{1}{2}I\omega^2 = \frac{1}{2}\frac{(I\omega)^2}{I} = \frac{|\vec{J}|^2}{2\mu R^2}.$$

This equation is fully general and applies to both the quantum-mechanical and classical cases. The quantized angular momentum resulting from Eq. (2) leads to

$$E_J = \frac{\hbar^2}{2\mu R^2}J(J+1). \tag{13.3}$$

Dipole selection rules dictate under what conditions molecules possessing a permanent dipole emit or absorb electromagnetic energy:

$$\triangle J = J' - J = \pm 1.$$

Hence, the absorption frequency in (3) is given as

$$\nu = \frac{E_{J'} - E_J}{h} = 2(J+1)B_e, \tag{13.4}$$

where $J' = J + 1$ and $B_e = h/(8\pi^2 I)$ denotes the rotational constant. This constant is closely related to the emission and absorption frequencies through Eq. (4). Whenever transitions occurring between the ground ($J = 0$) and first excited ($J = 1$) state are involved, Eq. (4) becomes particularly simple:

$$\nu = 2B_e.$$

This is why the signal associated with ν, as detected by radiotelescopes scanning interstellar clouds, approximately matches twice the value of the rotational constant B_e of molecules present in those clouds. However, this is so provided the far-infrared ($10^{11} - 10^{13}$ Hz) or the microwave ($10^9 - 10^{11}$ Hz) regions of the electromagnetic spectrum are involved, which approximately correspond to the rotation of small and polyatomic molecules, respectively.

It should be stressed that Eq. (3) was obtained by making the rigid rotor approximation, i.e. the vibrations of the system are disregarded. The true motion is of a more complex nature where centrifugal effects and coupling to nuclear vibrations have to be accounted for. Accordingly, the rovibrational energy would be given as

$$
\begin{aligned}
E_{v,J}(\nu) &= (v + \frac{1}{2})\nu - \nu\chi_e(v + \frac{1}{2})^2 + B_e J(J+1) \\
&- DJ^2(J+1)^2 - \alpha(v + \frac{1}{2})J(J+1),
\end{aligned}
$$

where the first term gives the well-known harmonic oscillator contribution, and the other four correspond to the so-called anharmonic correction, the one in Eq. (3), the centrifugal distortion and the vibrational-rotational coupling, respectively.

13.3 The Mysterious X-Ogen Line

In June 1970, radioastronomers D. Buhl and L. E. Snyder [2], while searching for hydrogen cyanide (HCN), discovered a new spectral line of very high intensity located at 89.19 GHz. This discovery was made through the 36-foot telescope of the National Radio Astronomy Observatory (NRAO) in Tucson, Arizona. They were able to detect this signal from five galactic sources: Orion, W3(OH), L134, Sgr A and W51. Since it was not possible to make a positive spectral identification, they called it X-ogen, meaning that it had an unknown extraterrestrial origin. The accuracy of the observation was 2 MHz, that is, X-ogen could be observed in the range 89.19 ± 0.002 GHz.

The discovery was presented the same year (1970) at the IAU General Assembly in

Brighton. Several molecules were proposed as candidates: The first one was hydrogen isocyanide HNC, suggested by G. Herzberg, apparently in the same meeting. The main argument was based on the fact that HCN and X-ogen are often found in the same cloud and thus, being HNC an isomer of the former, it was naturally expected to be also there.

Another proposal was HCO^+, due to William Klemperer [3], where the molecular ion is assumed to be linear. Klemperer thus used CH distance in HCN (1.06Å) and CO distance in CO^+ (1.115Å) in order to calculate the rotational constant of HCO^+, obtaining a very good result: $B_e = 44.623$ GHz. This corresponds to a transition frequency of 89.246 GHz which exhibits a deviation of only 0.06% off the observed value.

Other proposed candidates were: H_2S by Snyder, although this was immediately dropped in the same publication where they reported the discovery of the X-ogen line. CCH was proposed by J. Barshun [4] where, through a quantum chemical calculation, he obtained a transition frequency of 88.9 GHz. Yet another one was the proposal of Lovas [5]: a transition frequency ($J = 2 \rightarrow 1$) of 88.96 ± 3.2 GHz, associated with SiC molecule.

Out of all these proposals Klemperer's was undoubtedly the most interesting. In order to better understand the latter it is necessary to reproduce the calculation: The moment of inertia of a linear triatomic molecule is given by the formula

$$I = \frac{m_1 m_2 r_{12}^2 + m_1 m_3 r_{13}^2 + m_2 m_3 r_{23}^2}{m_1 + m_2 + m_3}, \tag{13.5}$$

whereas the rotational constant can be written as

$$B_e = \frac{h}{8\pi^2 I}. \tag{13.6}$$

If we assume the same distances proposed by Klemperer $r_{12} = 1.06$Å, $r_{23} = 1.115$Å and we take the atomic masses in HCO^+ as: $m_1 = 1.00977$ amu, $m_2 = 12.01115$ amu and $m_3 = 15.993$ amu, we obtain a transition frequency $\nu = 2B_e = 89.194828$ GHz. This result turns out to be far better than it was expected. In fact, the result is so good that some cancellation of terms must clearly be occurring, since such a simple calculation on the rotational constant cannot be that accurate. Therefore it is necessary to determine the most important corrections that must be made in the calculation of B [Townes and Schawlow]:

$$B = B_e - \sum_i \alpha_i \left(v_i + \frac{d_i}{2} \right) - J(J+1)D.$$

Unfortunately, in order to accomplish this goal a surface potential would have to be generated, i.e. we must first solve the Schrödinger equation for the electronic motion, and from this potential surface obtain the rovibrational constants α_i. Later we will discuss some results where these calculations have been addressed. Now we would like to discuss another interesting aspect in Klemperer's calculation.

The moment of inertia of a linear triatomic molecule is determined by two internuclear distances and the masses of the atoms. We can fix the moment of inertia−which is equivalent to fix the rotational constant−and to choose reasonable internuclear distances in such a way that we always get $\nu = 89.19$ GHz. Accordingly we can obtain the values shown in Table 1.

Table 1
INTERNUCLEAR DISTANCES OF HCO$^+$
THAT GIVE THE X-OGEN LINE

	d_{CO} (Å)	d_{CH} (Å)
1	1.100	1.1363
2	1.102	1.1264
3	1.104	1.1164
4	1.106	1.1063
5	1.108	1.0962
6	1.110	1.0860
7	1.112	1.0757
8	1.114	1.0654
9	1.116	1.0550
10	1.118	1.0446

All values in this table closely reproduce the X-ogen transition frequency $\nu = 89.19$ GHz. In particular, those hypothesized by Klemperer ($d_{CH} = 1.06$Å and $d_{CO} = 1.115$ Å) would be found between the 8th and 9th position. On the other hand, from a chemical point of view, another possible choice of internuclear distances could be $d_{CO} = 1.128$Å and $d_{CH} = 1.131$Å which correspond to internuclear distances in CO and CH$^+$. The result obtained is $\nu = 85.67688$ GHz, which is too far from the observed frequency. This example shows one of the typical pitfalls one may run into when arbitrarily extrapolating distances from one molecule to another. The calculation of the rotational constant of a molecule thus requires utilizing highly

accurate internuclear distances, especially due to the sensitivity displayed against small variations in the latter.

The correct procedure is to perform an optimization of the molecular geometry by means of quantum chemical methods. By using extensive CI (Configuration Interaction) calculations for HCO^+, Wahlgren et al. [6] obtained $d_{CO} = 1.1045$Å and $d_{CH} = 1.095$Å, which yields a transition frequency of $\nu = 89.36$ GHz that includes an anharmonic correction of 0.19 GHz. This result, although reasonably accurate, is not yet good enough to ensure that X-ogen is HCO^+.

In 1975 R. Claude Woods et al. performed the corresponding microwave experiment to obtain the rotational spectrum of HCO^+, where they found $\nu = 89188.545 \pm 0.020$ MHz. This clearly showed that X-ogen is HCO^+.

In 1976, W. P. Kraemer and G. H. F. Diercksen [8] reported quantum-chemical calculations on HCN and HCO^+. By means of techniques similar to those employed by Wahlgren et al., they obtained a frequency of 89.61 GHz, which is still far from the X-ogen line. However, based on the fact that HCN is a well known molecule from the experimental point of view, they deduced an empirical rule to estimate errors on the calculation of interatomic distances and force constants for that molecule. By extrapolating this empirical rule to HCO^+ and its isotopes they were able to obtain the exact X-ogen frequency, 89.19 GHz. They determined also the corresponding frequencies of the isotopes: $D^{12}C^{16}O^+$ (71.98 GHz), $H^{13}C^{16}O^+$ (86.76 GHz) and $H^{12}C^{18}O^+$ (85.17 GHz). These are to be compared with the ones actually observed in the interstellar space: $H^{13}C^{16}O^+$ with $\nu = 86.754$ GHz [9], $D^{12}C^{16}O^+$ with $\nu = 72.039$ GHz [13], and $H^{12}C^{18}O^+$ with $\nu = 85.162$ GHz [14].

Another important attempt to elucidate the nature of X-ogen was made by Herbst and Klemperer [10]. They estimated the rotational constant in an indirect fashion, involving one of the isotopes of HCO^+: $H^{13}CO^+$. In fact, a preliminary value for the transition $J = 1 \rightarrow 0$ on this molecular ion had previously been obtained, which prompted an intensive search of this line by Snyder and Buhl [11]. Years later, the line was observed at 86.754 GHz by Snyder et al. [9].

Despite the number of studies in the literature, as mentioned in the above discussion, the theoretical analysis of interstellar molecules based on quantum chemical methods still remains at an early stage of development, as pointed out by Arnau et al. [12]. In particular, the molecular treatment of the rotational spectrum ought to be based on

first principles (ab initio methods) to ensure the necessary accuracy. The ever higher precision achieved on radiotelescopic and experimental measurements should prompt parallel improvements and refinements on the numerical methods of computational quantum chemistry.

13.4 MgCN Molecule

The discovery of MgCN, the first magnesium-containing molecule detected in outer space, was made by Guélin et al. [15] and the molecular species was later identified in a microwave experiment by Kawaguchi et al. [16]. At the beginning several other molecules were proposed as candidates of the new detected line, based on the calculations of Largo-Cabrerizo et al. [17-19] and Fan and Iwata [20]. Eventually, all of these these candidates were ruled out in light of the experiment carried out by Kawaguchi et al. [16].

The first quantum chemical study on this species was done by Bauschlicher et al. [21], one year prior to its discovery in the circumstellar medium. They predicted MgNC to be a more stable molecule than MgCN, upon calculation of the dissociative process into the constituents Mg and CN. More recently, Ishii et al. [22, 23] performed the geometry optimization of MgNC, MgCN and the transition state between them. They also calculated a three-dimensional potential energy surface around the global minimum of MgNC, from which they derived a rotational constant of 5939.7 MHz. By following an alternative method proposed by Carter et al. [24], they were able to obtain an even better value: 5975.2 MHz.

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Table 2
OPTIMIZED GEOMETRY AND ROTATIONAL
CONSTANT OF MgNC

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Authors	$r(MgN)$	$r(NC)$	$B_o(MHz)$
Guélin et al. (1986)	—	—	5966.82
Kawaguchi et al. (1993)	—	—	5966.90
Bauschlicher et al. (1985)	1.9579	1.1642	5920.70
Ishii et al. (1993)	1.9451	1.1703	5939.70
Ishii et al. (1994)	1.945	1.170	5975.20
Kieninger et al. (1998)	1.9408	1.1727	5950.60
Palma et al. (1998)	1.9458	1.1590	5971.52

In Table 2 all calculations performed on this molecule, together with those recently obtained by the present author and collaborators [25, 26], are presented.

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