

Vibration frequencies for searches of free triatomic molecules in interstellar space

R Hefferlin and J Barrow

Southern Adventist University, Collegedale, Tennessee 37315, USA

E-mail: hefferln@southern.edu

Abstract. More and more cold interstellar molecules are being discovered, the majority of them being organic. Perhaps it is time to consider the numerous small molecules that also await observation. We report progress in tabulating symmetric-stretch vibration frequencies for neutral main-group ground-state triatomic molecules, formed from period-2 atoms, which are not yet studied.

1. Introduction

This investigation presents data that can be used in searches for free triatomic molecules that might exist in interstellar space. It is assumed that any combination of three neutral main-group atoms can form a cold molecule that could exist in circumstellar regions. Considerations such as bond types; bond orders; spin multiplicities; and chemical or radioactive reactivity are ignored in this study. The work pertains only to molecules all of whose atoms are from period 2; much more remains to be done.

2. Theory

The ability to visualize the mathematical space in which triatomic molecules exist is essential for understanding what follows in this paper. First, imagine an $8 \times 8 \times 8$ -atom cubical subspace populated by main-group period-2 atoms with rare-gas molecules on three faces. Then generalize to many such cubes, ranging from $(R_1, R_2, R_3) = (2, 2, 2)$ to $(7, 7, 7)$, where R_i is the period number of atom i (figure 1). The diagram is symmetric with respect to reflection in a plane containing the closest and the farthest edges of the figure; hence, for example, the cube with periods $(R_1, R_2, R_3) = (4, 2, 2)$ contains the same molecules as does the cube $(2, 2, 4)$. Aside from such subspaces where $R_1 \neq R_3$, there are 49 cubes with $R_1 = R_3$, each containing $\{[(8 \times 9)/2] \times 8\}$ non-redundant molecules.

3. Data acquisition

3.1. Simple molecular mechanics

Comparison of the symmetric-stretch vibration frequency of a linear, symmetric, triatomic molecule ABA and the vibration frequency ω_e of a diatomic molecule BA (which may be given in handbooks [1,2]) shows that ν_1 for these particular molecules can be obtained by

$$\nu_1 = \omega_e \sqrt{\mu/m} \quad , \quad (1)$$

Where μ is the diatomic reduced mass and m is the mass of either of the outer atoms.



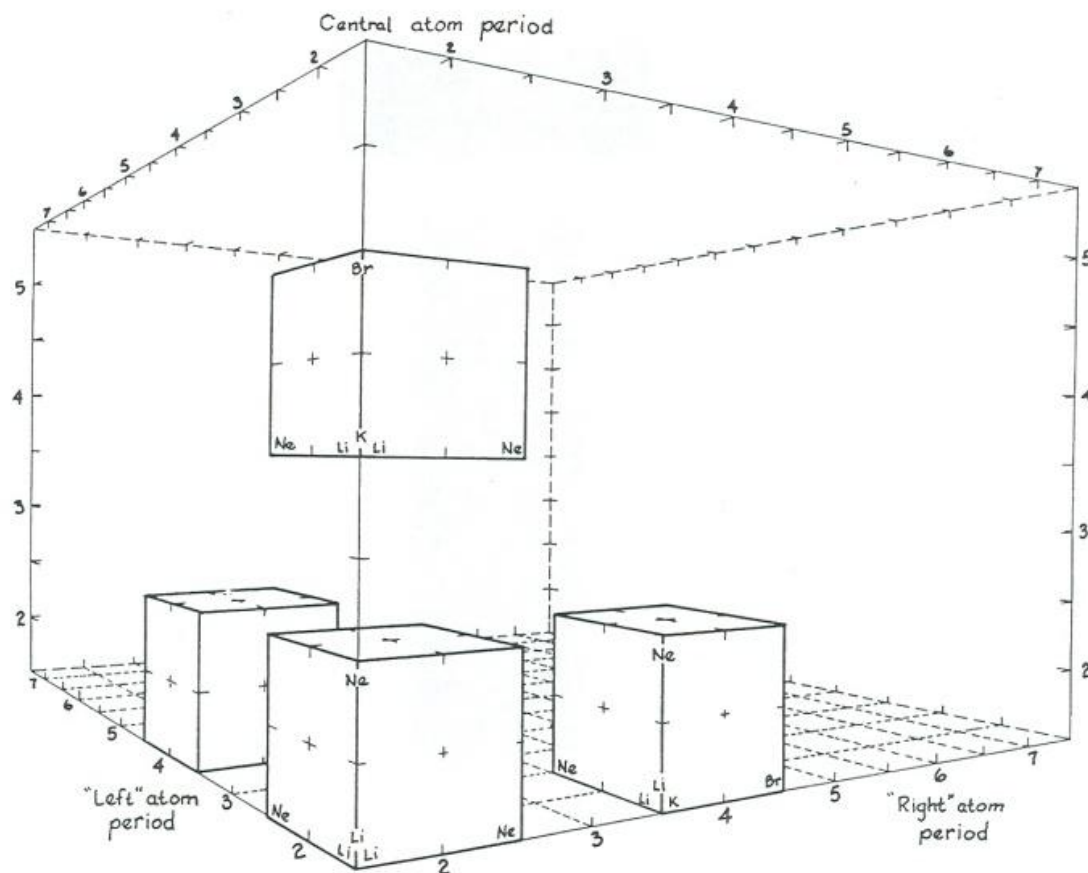


Figure 1. The formal space for main-group triatomic molecules showing selected cubical subspaces. R_1 , R_2 , and R_3 are the period numbers for the atoms on the “right” ends, centers, and “left” ends of the molecules in the cubical subspaces. Within each cube, the group numbers C_1 , C_2 , and C_3 (1 to 8) are defined similarly. This figure includes triatomics formed from atoms $(R_1, R_2, R_3) = (2, 2, 2)$ to $(5, 5, 5)$; species from $R_2 = 6$ and 7 lie higher above the figure; hydrogen and helium ($R_i = 1$) are not included in this study.

3.2. Computations

Two *ab initio* molecular modelling programs, QChem and PSI4[3], and the WebMo graphical user interface, were employed. Several basis sets were used: aug-cc-pVDZ, -pVTZ infrequently, -PVQZ; 6-311+G** and +G(d,p); and 6-31G(d) infrequently.

4. Results

As data for a given (R_1, R_2, R_3) were acquired, they were placed in bins of constant total electron count n_e , and then in order of increasing central-atom group number. The data for each molecule having more than one entry were averaged and assigned absolute and percent errors based on half the difference (for two entries), or based on the sample standard deviation. Table 1 contains the results.

Column 6 contains a code for the method(s) used to obtain each datum. Computer basis sets are **A**, aug-cc-pVDZ; **C**, aug-cc-pVQZ; **D**, 6-311+G**;**L**, 6-31G(d); and **M**, 6-311+G(d,p). The table of diatomic molecular data for use with equation (1) is **H** [2]. “**AC3G**” means computations based on basis sets **A** and **C** were each successful once and basis set **G** was successful three times. The small number of molecules listed in table 1, compared to the large count suggested by Section 2, is due to (a) only molecules *not* found in tabulations are included; (b) computations usually failed to produce meaningful molecular structures and frequencies for these unknown molecules; (c) ω_e that could be used to calculate ν_1 for unknown triatomic molecules using Equation (1) are not numerous.

Table 1. Data for molecules from $(R_1, R_2, R_3) = (2, 2, 2)$ in order of n_e and then C_2 . The averages are derived from computed values. If two sources contributed, then the half-difference error is shown in column 4; if more contributed, then the sample standard deviation is shown. In cases when one computation gave results so discrepant from the others that it caused percent errors of over 10%, it was discarded. All values are rounded to one significant figure after the decimal.

n_e	Species	Average ν_1 (cm ⁻¹)	Difference error, or σ	Percent error, or σ	Basis set
11	LiBeBe	388.4			C
12	BeBeBe	539.5	1.5	0.3	AD
	LiBeB	388.4			D
	LiBBe	533.2	0.2	0.0	2C
	LiCLi	570.9			A
13	BBeBe	443.8			M
	LiCBe	626.3			M
	LiNLi	772.8			A
14	BBeB	762.2			A
	BeBB	635.4			A
15	BBeC	534.6			A
	BBB	535.3			H
	BeCB	1218.6	0.3	0.0	CD
	BeNBe	1290.3	2.0	0.2	2D
	BNLi	764.1	2.8	0.4	AD
	BeOLi	840.1			C
	LiFLi	672.2			H
16	CBeC	1130.0	1.3	0.1	CD
17	BBeO	475.4 ^b			L
	CBeN	760.8			A
	BeBeF	417.3			C
	BeBO	646.9	31.7	4.9	DM
	LiBF	243.3	21.9	9.0	AC3G
	CCB	1526.1			M
	BNB	1290.8			L
	LiCO	652.2			M
	BeOB	493.3			M

Table 1, continued

n_e	Species	Average ν_1 (cm ⁻¹)	Difference error, or σ	Percent error or σ	Basis set
18	NBeN	520.0			A
	BBO	617.5	48.7	7.9	CM
	BCN	806.5	64.2	8.0	ACM
	BOB	1113.0			M
	BeFB	19.4			M
	LiFC	605.0			M
19	LiOF	804.1			M
	BeON	1439.5			M
	BOC	1141.5			M
20	OBeO	1060.5			M
	COC	1096.1			M
21	OBeF	660.1			A
	NBF	980.4			A
	NCO	1398.7			A
	BNF	980.3			M
	CNO	1103.2			A
	BeOF	128.6	5.5	4.3	2A
22	NCF	1205.0			C
	BOF	1059.8			A
	NON	1076.8			A
24	FNO	945.4	0.6	0.1	D,M

Acknowledgement

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References

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- [2] Huber K P and Herzberg G *Constants of Diatomic Molecules* (New York: Van Nostrand Reinhold)
- [3] Turney A A *et al* 2012 *WIREs Comput. Mol. Sci.* **2** 556. (doi: 10.1002/wcms.93).