Information and Strategies of Molecular Diatomic Spectroscopy Data

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Abstract

The spectroscopy of diatomic molecules is an important research area in chemical physics due to its relevance in astro chemistry, combustion chemistry, and ultra-cold physics. However, there is currently no database where the user can easily retrieve, in a useful format, the spectroscopic constants of a given molecule. Spectroscopy is an important tool in the study of atoms and molecules, giving us an understanding of their quantized energy levels. This paper provides information and strategies to strengthen the connection between data producers (e.g. ab initio electronic structure theorists and experimental spectroscopists), data modelers (e.g. line list creators and others who connect data on one aspect of the molecule to the full energetic and spectroscopic description) and data users (astronomers, chemical physicists etc).

Keywords: *Spectroscopy, Diatomic, Electronic structure, Molecule, Rotational.*

I. INTRODUCTION

When it comes to getting information, we're in the midst of what's known as the "information revolution." Data must be freely accessed and quickly exchanged among users in today's world. Data must also be presented in an engaging and user-friendly manner. As a foundation for societal progress, science must be current in that worldview. Chemical physics, in particular, is moving in that direction already. There are a number of valuable databases that have been made available to the public through various websites, including HITRAN and ExoMol. The spectral features of molecules important to applications in astrophysics and atmospheric physics are the emphasis of these sites; however, no information on the spectroscopic constants of diatomic molecules is provided on these sites.

Spectroscopy is a branch of physics that studies how electromagnetic radiation interacts with matter. It is possible for certain frequencies of photon emission to occur when light interacts with certain atoms and molecules. These frequencies rely on the spacing of the energy levels involved in the photon emission. These levels of atoms and molecules can be studied using this method.

Atoms and molecules more complicated than hydrogen have wave functions that can't be solved analytically. Diatonic molecules' energy transfers from one state to another, from vibrational to rotational, make an excellent starting point for studying and forecasting energy levels. The molecular orbitals of electrons remain unchanged by these changes.

II. DIATOMIC MOLECULAR SPECTROSCOPIC DATA

A flowchart depicting the interconnectedness of data kinds is shown in Figure 1. Experimental spectroscopy, ab initio electronic structure theory, a consolidated experimental spectroscopic network, line list generation, and cross-sections are the five primary types of data available.

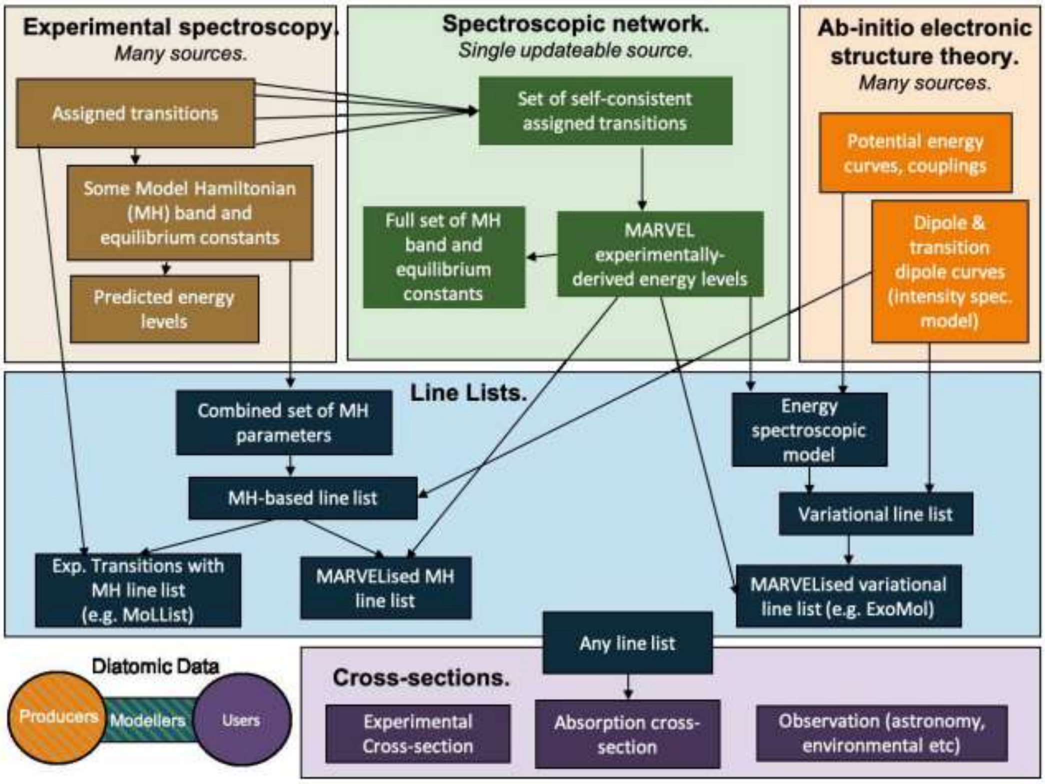

Figure 1: Connection between common types of diatomic molecular spectroscopic data

2.1 Assigned Experimental Transitions

A transition frequency between an initial and final quantum state, specified with approximate quantum numbers and preferably an uncertainty, constitutes an assigned experimental transition. It's common to see experimental publications that include data on one or more molecules and the ascribed rovibronic transitions in one or more spectral bands. The molecule's energy and spectroscopic characteristics can be seen through assigned spectrum transitions.

There is a growing trend of collating data from spectroscopic networks rather than individual studies (the primary source of data) (see below). In the past, this sort of data was typically compiled as experimental line lists, which lacked self-consistency and often failed to attribute specific data sources.

2.2 Consolidated Experimental Spectroscopic Network

A significant number of empirically assigned transitions with uncertainties and the accompanying inverted energy levels with uncertainties that are obtained experimentally. MARVEL compilation and analysis is commonly used to create spectroscopic networks (after the key enabling program). Using the MARVEL software programme, process data from multiple sources to produce a self-consistent spectroscopic network by increasing uncertainties and removing transitions as needed, ensuring the self-consistency of the entire spectroscopic network. This involves:

1. a thorough review of the literature;
2. digitization; and
3. consolidation of all available assigned transitions into a single format.

Modern database and accessibility standards are implemented across the MARVEL online domain. MARVEL datasets should be updated as soon as new experimental data becomes available, so that it may be utilized for cross-validation as well as line list updates. It is much easier to complete this activity because MARVEL is available online and can be done using a graphical user interface. The assistance of a more knowledgeable colleague during the learning process can't hurt.

Alternately, well-formatted text data in the MARVEL format and an email to the original compilation writers may typically be used to contribute new material as extra information instead.

2.3 Line Lists

For the most accurate representation of spectroscopy, use a line list, which includes all of the molecule's energies as well as all of its frequency and intensity transitions. For absorption cross-section prediction and as an input to complex gaseous environment models (e.g. radiative transfer), line lists are commonly utilised. Calculating molecular thermodynamic parameters like partition functions, specific heat, and cooling functions may be done with line lists as well.

Figure 1 depicts the five different types of line lists that may be constructed, each of which is distinguished by

- These are frequently referred to as perturbative and variational line lists. • The source of the interpolated and extrapolated energy levels and transitions - model Hamiltonians (MH) or energy spectrumocopic model (ESM);

- Whether MARVEL energy levels and/or experimental transitions are used to replace modeled energy levels.

One possible, yet-to-be-created line list uses MARVEL energies where they are accessible, as well as MH and ESM energies where they are dependable. When it comes to calculating diatomic line lists, LEVEL has long been the go-to tool. For this reason, it is being phased out by DUO, which tackles this coupling in an entirely different way. To construct a final line list, both programmes solve the Schrodinger equation to convert an ESM to a collection of energy levels, and then merge the rovibronic wave function data with the intensity spectrum model.

As new sources of ab initio energetic data and/or assigned experimental transitions become available, line lists should be continuously updated. A line list should be supplied as supplemental material to published publications, such as LEVEL or DUO input files and the energy and intensity spectroscopic models used to generate them. The corrected and original data should be kept when experimental corrections are applied to compute data.

2.4 Ab initio Energetic Data

Quantum chemistry electronic structure calculations were used to produce data that can be used to calculate the energies of rovibronic quantum states in diatomic molecules using a specific model and basis set. Potential energy curves and diagonal and off-diagonal spin-orbit coupling curves are the most essential energetic data (or at least their equilibrium values).

Best evidence [27] for several low-lying electronic states comes from MRCI calculations using orbitals from state-selective or state-averaged computations of the Complete Active Space Self-Consistent Field (CASSCF). A spin-symmetry with little multi-reference feature in its lowest lying electronic state may generally be extrapolated using CCSD(T) and basis set extrapolation.

Energy spectroscopic models and line lists are typically based on refined or raw ab initio energetic data. Studies of dynamics, such as molecular dynamics, rely on ab initio coupling and potential energy curves in addition to the construction of line lists.

Most potential energy curves and associated energetics data are now scattered throughout a large number of different articles. As a result, a large number of these articles simply include figures or constants, not raw data. The Computational Chemistry Comparison and Benchmark Database have diatomic ab initio vibrational frequencies for a variety of model chemistries (CCCBDB).

2.5 Cross-sections

Given environmental circumstances, the strength of absorption with respect to frequency or wavelength (temperature, pressure, resolution)

There are several studies in the literature that use cross-sections as illustrations to illustrate molecular constants rather than the underlying data that is usually recorded for larger molecules. The right software (e.g. Exocross for ExoMol formatted line lists) may generate modeled cross-sections from line lists at various temperatures and pressures. Line-broadening parameters can be used to estimate the resolution of experiments or observations.

This data format, which has a strong connection to observable data, can assist in the understanding of model spectroscopy by providing meaningful cross-section visualizations. If you're looking to find out which spectral area has the highest absorption for a certain compound, a cross-section plot is the best approach to do it.

III. ENERGY SPECTROSCOPIC MODEL (ESM)

In nuclear motion programmes such as LEVEL or DUO, the set of potential energy and coupling curves may be utilized to construct rovibronic energy levels for molecules. For the most part, energy spectroscopic models are based on empirical data.

With the use of parameterized potential energy curves and couplings (typically derived from ab initio energetics data), LEVEL and DUO may generate an energy spectroscopic model with excellent accuracy. The most typical application of an ESM is to generate a list of lines. As a result, ESMs may be utilized instead of ab initio energetics data in a number of different applications, such as simulations of reaction dynamics, where they can be more accurate than raw ab initio data.

Variationally-produced ExoMol line lists now include this information. Older line lists or line lists created using alternative approaches typically lack this data, which limits their usability for specific applications and makes future line list upgrades more difficult.

IV. INTENSITY SPECTROSCOPIC MODEL (I.E. DIPOLE AND TRANSITION DIPOLE MOMENTS)

The intensity of spectral transitions in a chemical line list is determined by combining the dipole moment curves with an ESM. Experimentation is nearly never used to get intensity information; instead, it is derived solely from the ab initio calculations outlined above.

It is difficult to derive experimentally precise absolute intensities. Models may be validated by comparing laboratory results to real-world data, such as astronomical spectra. Experiments on excited rovibronic states can also directly verify the model's absolute intensity.

ExoMol line listings now incorporate intensity spectroscopic models on a regular basis. In the literature, dipole and transition moments are distributed. In many cases, data is only available as numbers, making it difficult to make sense of. New dipole moment curves may be added to line lists easily. Relative intensity of bands can be corrected, but only after careful consideration and good documentation.

V. ROVIBRONIC ENERGY LEVELS

Quantum numbers that approximate rovibronic state energies (often in relation to the molecule's lowest energy quantum state and preferably with errors) There are a number of methods for obtaining the most precise energy levels, but the most exact one is inverting the self-consistent MARVEL transition frequencies. There are other methods for determining rovibronic energy levels, such as calculating the nuclear motion Schrodinger equation for a certain energy spectroscopic model.

Common use:

- To enable fitting of the energy spectroscopic model;
- To replace modeled energy levels in a line list and thus enable high precision frequency predictions.
- **Model Hamiltonian Parameters (e.g. Band and Equilibrium Constants)**

In order to calculate the energy of a molecule's quantum states, a set of parameters are utilized. You may get reasonable functional forms for the dependence on molecular quantum numbers of diatomic energy levels (and consequently transition frequencies) by approximating the entire system Hamiltonian, which is to say using a model Hamiltonian (e.g. a rigid rotor or Morse oscillator). Using these formulas, you may tweak the parameters to get the best match between the expected and observed transition frequencies.

Tv and Bv band constants are the most commonly used parameters for fitting rotational levels inside a single vibrational state of an electronic state and equilibrium constants (Te and Be and De) for fitting rotational levels from multiple vibrational levels of an electronic state. The spin-orbit coupling, A, is also critical for states with nonzero angular momentum and spin. The spin-spin and spin-rotation couplings, as well as off-diagonal couplings between electronic states, are crucial for high-accuracy applications.

The community standard software for fitting observed spectral transitions to Hamiltonian models is PGopher, which can be found on nearly every computer in the world today. The electrical structure of a molecule may be summarized in this way, which is adequate for many purposes. A partition function may be calculated by using this tool.

Because of the high connection between electronic states, molecular constants are troublesome when the quantum energy levels are perturbed. Variational techniques based on fitted energy spectroscopic models are more accurate in predicting energy levels and spectra than those based on chemical constants.

HH from 1979 remains the strongest compilation to date. The Diatomic Molecular Spectroscopy Database (DMSD), which complies to contemporary database standards, is the best place to get much of this information. Furthermore, DMSD may be updated by the community; the addition of molecular constants post-1979 into DMSD is a critical priority in diatomic data collation. Band constants are more accurate than equilibrium constants, despite the fact that they are not kept in a central database. PGopher input files should be centralized, and authors should be properly credited. This is the quickest method to go ahead. The DMSD website, for example, might make this information available online when it has been entered into a SQL database.

VI. CONCLUSION

There are several sources of information that have not yet been added into big databases, such as pre-dissociation and reaction rates, that may be of interest to data consumers. The collection of all spectroscopic data on a single diatomic can be time-consuming and needs expertise to guarantee that all relevant data is included in the compilation. As a result, maintaining an up-to-date and comprehensive collection of literature on each molecule is a valuable endeavor, but one that is difficult to justify on its own.

REFERENCES

1. Hanson, Ronald & Spearrin, Raymond & Goldenstein, Christopher. (2016). Diatomic Molecular Spectra. 10.1007/978-3-319-23252-2_2.
2. Falaye, Babatunde & Ikhdair, Sameer & Hamzavi, Majid. (2015). Spectroscopic study of some diatomic molecules via the proper quantization rule. Journal of Mathematical Chemistry. 53. 10.1007/s10910-015-0491-9.
3. Parigger, Christian & Woods, Alexander & Surmick, David & Gautam, Ghaneshwar & Witte, Michael & Hornkohl, James. (2015). Computation of diatomic molecular spectra for selected transitions of aluminum monoxide, cyanide, diatomic carbon, and titanium monoxide. Spectrochimica Acta Part B: Atomic Spectroscopy. 107. 10.1016/j.sab.2015.02.018.
4. Tiemann, Eberhard & Knöckel, Horst. (2013). Renaissance in diatomic spectroscopy. AIP Conference Proceedings. 1545. 79-95. 10.1063/1.4815843.
5. Melo de Almeida, Marcos & Prudente, Frederico & Fellows, C. & Marques, J. & Pereira, Francisco. (2011). Direct fit of spectroscopic data of diatomic molecules by using genetic algorithms: II. The ground state of RbCs. Journal of Physics B: Atomic, Molecular and Optical Physics. 44. 225102. 10.1088/0953-4075/44/22/225102.
6. Saleh, Zeyad & AL-YASARI, RAJAA & Al-Amiedy, Dhia. (2011). Theoretical study of emission spectra for the isotopic molecule Lithium Li16H hydride. ATTI DELLA "FONDAZIONE GIORGIO RONCHI". ANNO LXVI. 819-824.
7. Parigger, Christian & Hornkohl, James. (2010). Diatomic molecular spectroscopy in laser-induced breakdown plasma. Int. Rev. Atom. Mol. Phys.. 1. 25-43.
8. Kowalczyk, Pawel & Wlodzimierz, JASTRZEBSKI & Pashov, A.. (2006). Exotic states of diatomic molecules and methods of their description. Optica Applicata. 36