Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules

Marilyn E. Jacox
National Institute of Standards and Technology
Gaithersburg, MD 20899

Abstract

The database concerned with the vibrational and electronic energy of polyatomic transient molecules with from 3 to 16 atoms now contains the experimentally determined vibrational fundamentals and electronic band origins of approximately 2,140 neutral and ionic transient molecules. This database is distributed in both published and computer-searchable forms. Emphasis is placed on species with lifetimes too short for study using conventional sampling techniques. The compilation also includes many high temperature molecules and several less reactive species which have presented spectral evaluation problems and which are important in a wide variety of environmental and industrial chemical systems. Radiative lifetimes and the principal rotational constants are given. Observations in the gas phase, in molecular beams, and in rare-gas and diatomic molecule matrices are evaluated. The types of measurement surveyed include conventional and laser-based absorption and emission techniques, laser absorption with mass analysis, and photoelectron spectroscopy.

Discussion

Transient molecules are important in a wide variety of chemical reaction systems, including those typical of combustion, plasma processing, chemical vapor deposition, decomposition of energetic materials, and environmental research and monitoring. A database concerned with critically evaluated vibrational and electronic energy levels of polyatomic transient molecules with from 3 to 16 atoms now contains the experimentally determined vibrational fundamentals and electronic band origins of approximately 2,140 neutral and ionic species. Emphasis is placed on molecules with lifetimes too short for study using conventional sampling techniques. These molecules include free radicals, molecular ions, and other short-lived reaction intermediates. The database is gradually being extended to include small high-temperature molecules. At this time, it contains spectroscopic information on many polyatomic oxides. Certain other especially important species that are difficult to isolate in pure form and have presented spectral evaluation problems, including OClO, HNCO, H_2O_2, *cis*- and *trans*- HONO, and $HONO_2$, are also included.

The focus of this database is on the spectroscopic properties of the species of interest under conditions of minimal interaction with other species. Thus, the most definitive data are those obtained in low-pressure gas-phase measurements, including studies of molecular beams. Also included are data for the molecule trapped in rare-gas matrices and/or in small molecule matrices such as H_2, N_2, O_2, CO, or CO_2. Matrix shifts for uncharged molecules and ionic species trapped in Ne are generally less than 1%, as are those of uncharged molecules trapped in Ar. H_2 is also a promising matrix material, but there are insufficient data for a satisfactory estimate of matrix shifts characteristic of molecules trapped in solid H_2. More polar matrix materials such as H_2O and the Freons are not

included, nor are data for high-temperature molecules in the solid state, which generally have very broad absorptions.

Many types of measurement are included in the database. Among these are conventional and laser-based absorption and emission techniques, laser absorption with mass analysis, and photoelectron spectroscopy.

As of 1 October 1997, earlier versions of the database were available both as a monograph [1] and as a computer-searchable database, VEEL 4.0 [2]. Spectroscopic data for 1,582 molecules are included in the monograph, and data for 1,796 molecules are included in VEEL 4.0. Both forms include excited-state band origins, ground- and excited-state vibrational fundamentals, and a full bibliography. The monograph also includes radiative lifetimes and principal rotational constants, cited to 0.001 cm^{-1}. The system requirements for VEEL 4.0 are an IBM[a] AT class or PS/2 personal computer (80286, 80386, 80486, or Pentium processor) with PC- or MS-DOS 2.1 or greater or with Windows 95, as well as 512 kilobytes of RAM and at least 4.0 megabytes of hard disk storage. VEEL 4.0 can also be used with Macintosh computers that have PC emulation software, and instructions for installing it on systems which use Windows NT are available.

Three new outputs which revise and extend the coverage of the database will soon become available. A supplement to the monograph [1] is to be published early in 1998 in the *Journal of Physical and Chemical Reference Data*. Version 5.0 of VEEL is to be released in late 1997. The December 1997 version of NIST Standard Reference Database 69 *(http://WebBook.NIST.gov)* is also scheduled to include the data contained in VEEL 5.0, searchable by vibrational and electronic energy levels, together with other molecular properties.

Acknowledgments

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Footnotes and References

[1] M. E. Jacox, "Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules," Monograph No. 3, *J. Phys. Chem. Ref. Data*, 461 pages (1994)

[2] NIST Standard Reference Database 26, NIST Vibrational and Electronic Energy Levels of Small Polyatomic Transient Molecules (VEEL), Version 4.0

[a] Certain commercial instruments and software are identified in this paper in order to specify adequately the range of utility of the VEEL data package. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the items identified are necessarily the best available for the purpose.